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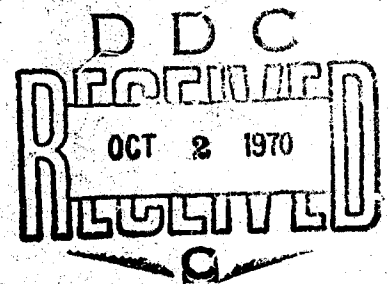# PERFLUOROALKYLENE OXIDE POLYMERS
AS HIGH-TEMPERATURE SEALANTS

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Minnesota Mining and Manufacturing Company

TECHNICAL REPORT AFML-TR-70-85

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Air Force Materials Laboratory
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

PERFLUOROALKYLENE OXIDE POLYMERS

AS HIGH-TEMPERATURE SEALANTS

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FOREWORD

The work described in this report was performed by the 3M Company under Contract No. F33615-68-C-1362. This contract was initiated under Project 7340, "Nonmetallic and Composite Materials," Task 734005, "Elastomeric and Compliant Materials," and administered by the Elastomers and Coatings Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, with Mr. John W. Spence and Mr. Thomas L. Graham as project engineers. Previous reports were described under Contract Nos. AF 33(615)-1658 and AF 33(615)-5148.

The experimental work described in this report was carried out by Dr. James R. Throckmorton, Project Coordinator, and Dr. Paul H. Ogden, assisted by Mr. Merritt L. Stigen and Mr. James H. Jansen, with program direction under Dr. R. A. Mitsch (1 June 1968 - 31 December 1968) and Dr. G. H. Crawford (1 January 1969 - 30 November 1969).

The report covers work conducted from 1 June 1968 to 30 November 1969.

This technical report has been reviewed and is approved.

WARREN P. JOHNSON, Chief
Elastomers and Coatings Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

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ABSTRACT

Ph>tolysis of perfluoroether diacid fluorides and chain-extensicn of fluorocarbon ether-bridged chlorosilanes have been investigated as routes to a high-temperature integral fuel tank sealant polymer.

Photolysis of perfluoroether diacid fluorides has been found to give two triacid fluorides by reaction of the initially formed photo-fragments with the monomer diacid fluoride. These triacid fluorides lead to large quantities of branched polymer and prevent formation of high molecular weight linear polymer.

Six different fluorocarbon ether-bridged chlorosilanes have been prepared and their polymerization to silanol-ended fluorocarbon ether-bridged siloxanes investigated.

Sealant compounds prepared from the siloxane polymers have long term stability in air up to 400°F. Substitution of tri-fluoropropyl groups on silicon is necessary to achieve the desired jet fuel resistance. Aging of two sealant compounds containing trifluoropropyl groups on silicon indicate that they will be useful for certain periods of time up to 500°F in a jet fuel environment. However, more research is necessary to firmly determine the upper temperature limit.

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I. INTRODUCTION

The objective of this program is to develop fluorocarbon ether based polymers for use in aircraft integral fuel tank sealant materials capable of service at temperatures ranging from -65° to 600°F and above.

Under Contract No. AF33(615)-1658,[1] linear perfluoroalkylene oxide polymers were prepared by the coupling of pure di-iodo-perfluoroethyl ether monomers as shown below.

$$ICF_2CF_2OCF_2CF_2I \xrightarrow{\ \ \ Hg\ \ \ } I(CF_2CF_2OCF_2CF_2)_nI$$
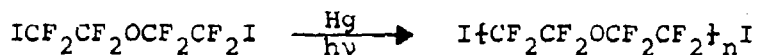
Although this polymer exhibited broad thermal properties (-65°C. to 700°F.) and solvent resistance, vulcanizates could not be prepared.

Work under a related Government contract[2] led to perfluoro-alkylene oxide polymers by means of the reaction:

$$O(CF_2CF_2\overset{O}{\overset{\|}{C}}F)_2 \xrightarrow{\ h\nu\ } F\overset{O}{\overset{\|}{C}}CF_2CF_2(O(CF_2)_4)_xOCF_2CF_2\overset{O}{\overset{\|}{C}}F + F\overset{OO}{\overset{\|\|}{CC}}F + CO + COF_2$$
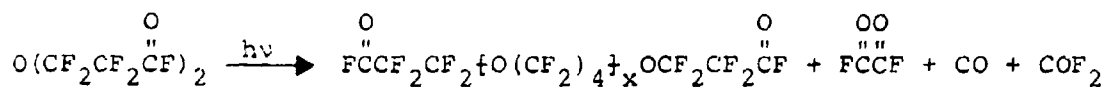
This reaction appeared to have certain process advantages over the iodide coupling method, and it was felt that by proper control of polymer molecular weight, type of termination, and degree of functionality, a high-temperature sealant material could be formulated. Thus, under a follow on contract,[1] No. AF33(615)-5148, and the current contract, polymers were prepared by photolysis of perfluoroether diacid fluorides, different functional groups were introduced, and potentially useful curing systems were investigated. Although the photopolymer and its derivatives could be

vulcanized, high yields of high molecular weight, linear photo-
polymer could not be prepared. As a result, efforts were shifted
to the synthesis of the type of polymers indicated below:

$$HO \left[\underset{\underset{CH_3}{|}}{\overset{\overset{R}{|}}{Si}} CH_2 \underset{}{\overset{\overset{R'}{|}}{CH}} (CF_2CF_2OCF_2CF_2)_n \overset{\overset{R'}{|}}{CH}CH_2 \underset{\underset{CH_3}{|}}{\overset{\overset{R}{|}}{Si}}O \right]_x H$$
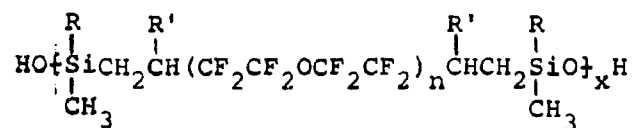
$$n = 1 \text{ or } 2$$
$$R = CH_3 \text{ or } CH_2CH_2CF_3$$
$$R' = H \text{ or } CH_3$$

This report presents the synthesis procedures used in preparing
the above indicated species of fluorocarbon ether-bridged siloxane
polymers and the properties of the resultant polymers and sealant
compounds. Results of efforts expended in understanding and
attempting to improve the photochemical technique for polymerizing
perfluoroether diacid fluorides are also presented.

II. DISCUSSION

A. FLUOROCARBON ETHER-BRIDGED CHLOROSILANES

Six different fluorocarbon ether-bridged monochlorosilanes were synthesized over the present reporting period. These monomers are conveniently divided into two closely related structural types, both

$$\begin{array}{ccc} R & CH_3 & CH_3 \ R \\ | & | & | \ | \\ ClSiCH_2CH(CF_2CF_2OCF_2CF_2)_nCHCH_2SiCl \\ | & | \\ CH_3 & CH_3 \end{array}$$
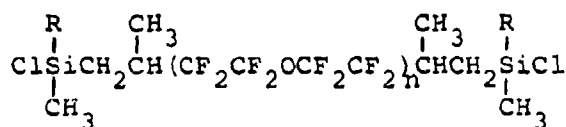
Type I   n = 1

R = CH_3 or $CF_3CH_2CH_2$

$$\begin{array}{ccc} R & & R \\ | & & | \\ ClSiCH_2CH_2(CF_2CF_2OCF_2CF_2)_nCH_2CH_2SiCl \\ | & & | \\ CH_3 & & CH_3 \end{array}$$
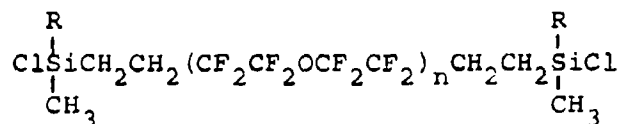
Type II   n = 1 or 2

R = CH_3 or $CF_3CH_2CH_2$

of which contain central perfluoroalkylene oxide moieties linked to terminal silicon through hydrocarbon insulating groups. As is well known, silicon must be separated from fluorine-substituted carbon atoms by at least two non-fluorinated carbon atoms in order to avoid a substantial reduction in the stability of the molecule.[3]

The initial synthetic effort on the fluorocarbon ether-bridged chlorosilanes was directed toward preparation of the dimethylchloro-silyl derivatives. However, as a result of the inadequate solvent

resistance of the polymers derived from these monomers, synthesis of the corresponding trifluoropropylmethylchlorosilyl derivatives was undertaken. The preparation of these monomers is discussed in the following paragraphs.

1. Bis-α,ω-[2-(Diorganochlorosil)-1-Methylethyl]Perfluoro-alkylene Oxides

The reactions used in preparation of monomers of type I are illustrated in the following equations:

$$O(CF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_3)_2 \xrightarrow{CH_3MgI} O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OH)_2$$

(I)

$$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}OH)_2 \xrightarrow{H_2SO_4} O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2)_2$$

(II)

$$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}{=}CH_2)_2 \xrightarrow[H_2PtCl_6]{R(CH_3)SiHCl} O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}H\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle R}{|}}{CH_2Si}}Cl)_2$$

$$R = CH_3 \text{ or } CF_3CH_2CH_2$$
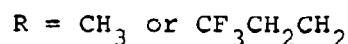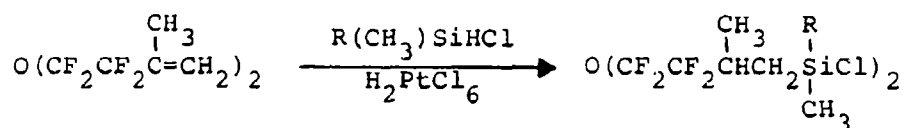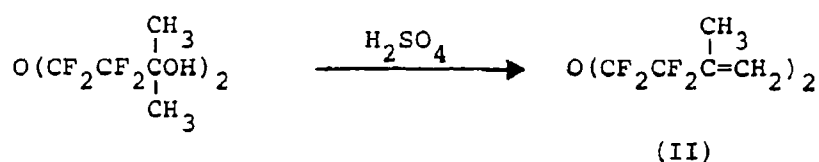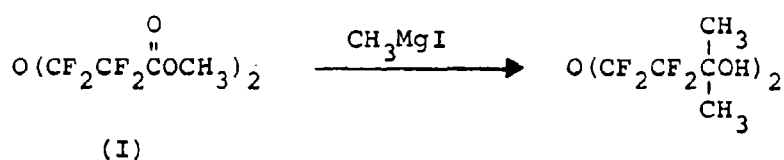
After some refinement of the reaction conditions, the type I monomers were obtained from dimethyl perfluorooxydipropionate (I) in overall yields of 55-77%.

The crude tert-alcohol obtained from (I) in the first reaction was never purified but instead reacted directly with 36N sulfuric acid. Dehydration of the alcohol with sulfuric acid appears ᴏ

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begin at about 100°C. as evidenced by the start of the formation of a layer on top of the reaction mixture. After about two hours and after the temperature of the reaction mixture has reached 150-165°C. dehydration is complete. The diene (II) is then separated from the sulfuric acid with a separatory funnel and pure (II) isolated by distillation in about 80-88% overall yield from (I). Dehydration of the _tert_-alcohol has also been achieved via pyrolysis of its acetate ester, but the yield of olefin is lower (55%) and the reaction less convenient than sulfuric acid dehydration.

Attempts to add organo-H-chlorosilanes to the above olefin (II) were preceded by attempts to add dimethylchlorosilane to $CF_3CF_2OCF_2CF_2C(CH_3)=CH_2$.

$$CF_3CF_2OCF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2 \xrightarrow[\text{catalyst}]{(CH_3)_2SiHCl} CF_3CF_2OCF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}Cl$$

(III)
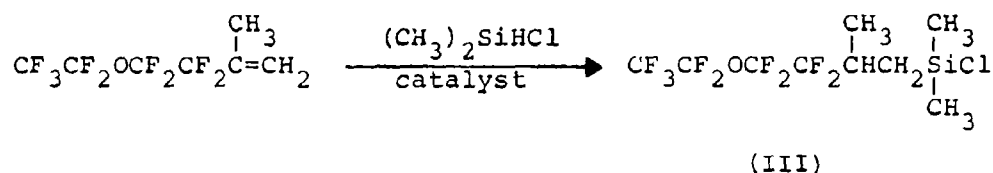
These preliminary reactions included heating the mixture of olefin and silane with platinum on charcoal catalyst and also with chloroplatinic acid catalyst at atmospheric pressure, and also with these same two catalysts in an enclosed system under pressure. Of these, only the reaction with chloroplatinic acid in an enclosed system was successful. The other reactions afforded little evidence of silane addition to the olefin.

In view of the above results, $O[CF_2CF_2C(CH_3)=CH_2]_2$ was reacted with dimethylchlorosilane and chloroplatinic acid catalyst in an enclosed system under pressure. This gave the desired di-addition product together with a quantity of the mono-addition compound.

$$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2)_2 \quad \xrightarrow[\text{H}_2\text{PtCl}_6]{(CH_3)_2SiHCl} \quad$$

(II)

$$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}Cl)_2$$

(IV)

+

$$CH_2=\overset{\underset{\displaystyle CH_3}{|}}{C}CF_2CF_2OCF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}Cl$$

(V)
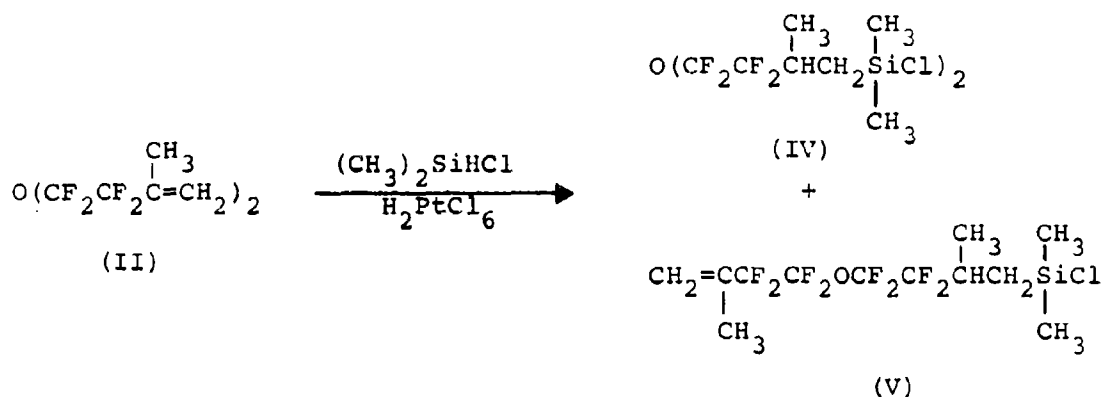
Examination of the effect of temperature on the yield of di-adduct showed that high yields may be obtained by reacting the olefin with excess organo-H-chlorosilane in a Hastelloy bomb at 150-175°C. In this way, the following type I silanes were prepared:

Compound	b.p./mm.	% Yield[*]
$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle\overset{\displaystyle CF_3}{|}\,\overset{\displaystyle CH_2}{|}\,\overset{\displaystyle CH_2}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}}Cl)_2$ (VI)	119°C/.01	55
$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}Cl)_2$ (IV)	90°C/.03	65
$O(CF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2\overset{\overset{\displaystyle CH_3}{|}}{Si}Cl_2)_2$ (VII)	98°C/.03	71

[*] Based on original number of moles of $O(CF_2CF_2CO_2CH_3)_2$ employed.

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In each case, any unreacted olefin and mono-addition product were recovered and reused. Products resulting from the "reverse-addition" of SiH to olefin were never detected in these reactions. The dichlorosilane (VII) was prepared for the purpose of converting it to an acetoxysilane curing agent and possible copolymerization reactions with the monochlorosilanes.

2. <u>Bis-$\alpha,\omega\{2$-(Diorganochlorosil$\}$Ethyl$\}$Perfluoroalkylene Oxides</u>

The reactions used in the preparation of monomers of type II are illustrated in the following equations:

$$(CF_2CF_2OCF_2CF_2\overset{\overset{O}{\|}}{C}OCH_3)_2 \xrightarrow[\overline{(CH_3)_2CHMgBr}]{CH_3MgI} (CF_2CF_2OCF_2CF_2\overset{\overset{OH}{|}}{C}HCH_3)_2$$

(VIII)

$$(CF_2CF_2OCF_2CF_2\overset{\overset{\overset{O}{\|}}{OCCH_3}}{\underset{|}{C}}HCH_3)_2 \xrightarrow{570\,°C} (CF_2CF_2OCF_2CF_2CH=CH_2)_2$$

(IX)   (X)

$$(CF_2CF_2OCF_2CF_2CH=CH_2)_2 \xrightarrow[H_2PtCl_6]{R(CH_3)SiHCl} (CF_2CF_2OCF_2CF_2CH_2CH_2\overset{\overset{R}{|}}{\underset{\underset{CH_3}{|}}{Si}}Cl)_2$$

$$R = CH_3 \text{ or } CF_3CH_2CH_2$$
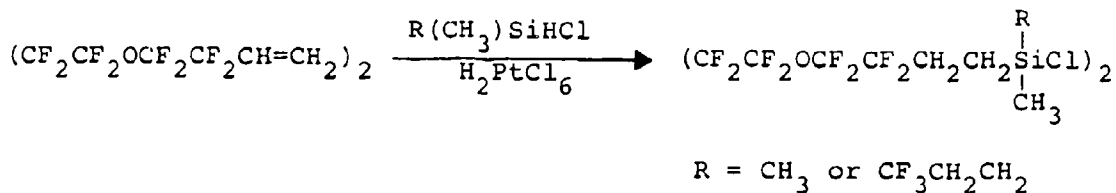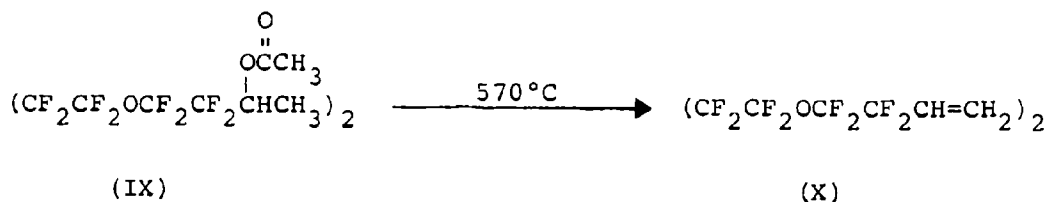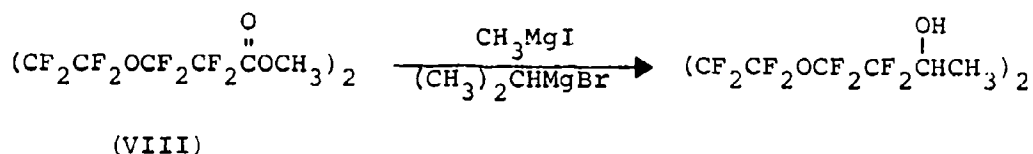
Dimethyl perfluoro-4,9-dioxadodecanedioate (VIII) was prepared by photodimerization of perfluorooxydipropionyl fluoride and reaction of the photoproduct with methanol. This reaction is discussed in

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$$O(CF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}F)_2 \quad\xrightarrow{\quad h\nu\quad}\quad (CF_2CF_2OCF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}F)_2$$
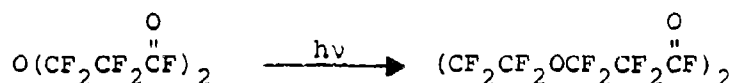
a subsequent section. Overall yields of the type II monomers from either dimethyl perfluorooxydipropionate (I) or dimethyl perfluoro-4,9-dioxadodecanedioate (VIII) were generally on the order of 10-20%.

The yields of the type II monomers were low primarily as a result of the large quantity of by-products formed in the first and third reactions illustrated above. Spectroscopic analyses of the products obtained from (I) in the first reaction indicate that the major by-product ($\sim$40% yield) contains the $-CH(OH)CH(CH_3)_2$ end-group, presumably formed by reaction of (I) with isopropyl magnesium halide and then reduction of the ketone with isopropyl magnesium halide. The desired reactions, formation of methyl ketone by reaction of (I) with methyl magnesium halide and reduction of the ketone with isopropyl magnesium halide, are apparently not favored and give the desired secondary alcohol in only 40% yield (established by chromatographic analyses on the acetate ester of crude alcohol).

Sulfuric acid dehydration of the mixture of alcohols from (I) was not successful. Large quantities of SiF_4 were evolved during the reaction and an intractable tar formed in the reaction flask. Attempts to distill $O(CF_2CF_2CH=CH_2)_2$ (XII) from the reaction as it formed also gave an intractable solid and no olefin. Phosphorus pentoxide dehydration did give (XII), but in less than 1% yield together with silicon tetrafluoride evolution and tar formation. Other workers have had a similar lack of success in attempting to dehydrate alcohols of this nature[4,5] and have found acetate ester pyrolysis to be the most satisfactory dehydration technique.[6]

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Application of the acetate ester pyrolysis technique to de-hydration of the secondary alcohols from (I) and (VIII) was success-ful. Pyrolyses of (XI) were conducted in a flow system. The

$$CH_3\overset{O}{\overset{\|}{C}}OCHCF_2CF_2OCF_2CF_2CHO\overset{O}{\overset{\|}{C}}CH_3$$
$$\quad\ \underset{CH_3}{|}\qquad\qquad\qquad\underset{CH_3}{|}$$

(XI)

$$CH_3\overset{O}{\overset{\|}{C}}OCHCF_2CF_2O(CF_2)_4OCF_2CF_2CHO\overset{O}{\overset{\|}{C}}CH_3$$
$$\quad\ \underset{CH_3}{|}\qquad\qquad\qquad\qquad\underset{CH_3}{|}$$
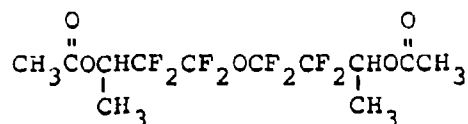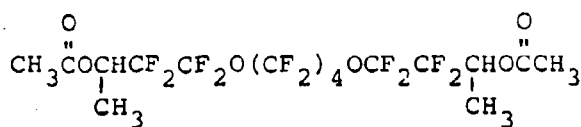
(IX)

acetate ester was slowly dripped into a nitrogen stream (400-500 cc/min) and swept onto small fish spines packed into a 550-650°C furnace consisting of a vycor tube (2.8 cm by 20 cm) wrapped with a heating wire encased in asbestos. The effluent pyrolysis products were then condensed into a series of traps cooled to -196°C. The pyrolysis products were separated from the unreacted and half-pyrolyzed material by transferral in vacuo to a vacuum system, washed with water, dried ($CaSO_4$) and (XII) isolated by distillation

$$CH_2=CHCF_2CF_2OCF_2CF_2CH=CH_2$$
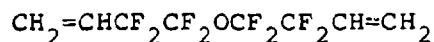
(XII)

(b.p. ca. 118°C). The results of several pyrolyses at different temperatures and nitrogen flow rates are summarized in Table I.

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TABLE I - Pyrolysis of $O[CF_2CF_2CH(O_2CCH_3)CH_3]_2$

Reaction[b]			Products (%)	
t, °C	Diacetate (g)	After water[a] Wash (g)	Yield	Conversion
520	7.0	0.2	4	18
550	9.5	0.45	7	30
575	7.3	1.9	39	60
610	11.5	6.2	78	95
650	9.8	4.5	65	70
550[c]	12.4	4.3	50	93
610[c]	14.6	8.7	87	-

a) This material is estimated to contain 75% (XII); b) Nitrogen flow ca. 500 cc/min except as noted; c) Nitrogen flow ca. 400 cc/min.

Prior to the pyrolysis of (IX), several preliminary pyrolysis reactions were conducted with (XI) and the acetate ester derived from methyl perfluorooctanoate. These pyrolyses were effected by dropping the esters into a furnace consisting of a 32 cm heated section of quartz tubes (3 mm by 10 mm) packed into a 60 cm by 2.8 cm vertical quartz tube rather than the previously described furnace. The reactions of (XI) are summarized in Table II and indicated that temperatures above 500°C should be used for the pyrolysis of (IX).

TABLE II [a] - Pyrolysis of $O[CF_2CF_2CH(O_2CCH_3)CH_3]_2$

Reaction[b]		Product[c] (%)			
t, °C	N_2 (cc/min)	Wt. Pyrolyzate (g)	Diene	Half-pyrolyzed	Unre-acted
500	25	1.4	40	40	20
535	25	1.7	50	-	-
535	10	1.6	55	-	-
550	10	1.4	65	-	-
550	25	1.4	79	18	3

a) Pyrolysis conditions are the same as used on (IX), Table III;
b) 2.0 g of diacetate added in 10-15 min.; c) Product analysis by
VPC area measurements on diene, half-pyrolyzed and unreacted
acetate esters.

Several small scale experiments (Table III) with (IX) in the
all quartz furnace indicated that satisfactory yields of diene (X)

$$CH_2=CHCF_2CF_2O(CF_2)_4OCF_2CF_2CH=CH_2$$
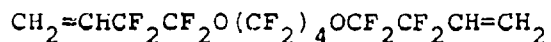
(X)

could be obtained by pyrolysis at 570°C in conjunction with a
nitrogen sweep rate of 10 ml/min and an acetate addition rate of
15 g/hr. Using these conditions and by repyrolysis of half-
pyrolyzed diacetate yields as high as 75% of isolable diene were
obtained.

TABLE III - Pyrolysis of $[CF_2CF_2OCF_2CF_2CH(O_2CCH_3)CH_3]_2$						
Reaction			Products [a] (%)			
Amt.(g)	t,°C	N_2 (cc/min)	Wt. Pyrolyzate (g)	Diene	Half Pyrolyzed	Unre-acted
2	535	10	1.7	70	26	4
2	550	10	1.6	82	16	2
2	550	25	1.6	92	10	0
1.8	570	10	1.4	98	2	0
30[b]	570	10	28.5	82	15[c]	2

a) Percentages are from VPC area measurements on diene, half-pyrolyzed and unreacted ester; b) Added over 2.25 hours.; c) Re-pyrolysis gave a 75% yield of isolable diene from this reaction.

Interestingly, attempts to apply the above pyrolysis conditions to the acetate derived from methyl perfluorooctanoate were less successful. The highest yields of olefin from this particular acetate were obtained by pyrolysis at 500°C. However, under all

$$CF_3(CF_2)_6\underset{\underset{CH_3}{|}}{CH}O\overset{\overset{O}{||}}{C}CH_3$$
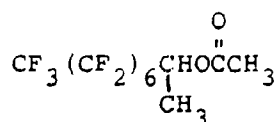
conditions employed the yield of olefin was disappointingly low (50% ly VPC analysis) and always contaminated by more than 10 in-separable decomposition products. The problems encountered are exemplified by the formation of only 20 g of olefin (VPC analysis) from pyrolysis of 112 g of acetate. The remaining product (53 g) contained about 10 different compounds. These results indicate that optimum pyrolysis conditions depend to a certain extent on the non-hydrocarbon portion of the molecule and thus can vary con-siderably from one compound to another.

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The chloroplatinic acid catalyzed reaction between dimethyl-chlorosilane and (X) and (XII) was first attempted at atmospheric pressure. In both cases, an exotherm occurred shortly after addition of the silane (ca. 30 min) indicating a reaction was taking place. After the exotherm, the mixture was heated at reflux overnight and then distilled. This gave negligible quantities of unreacted diene, no mono-addition product, the expected di-addition product and a lower boiling fraction which contained a substantial quantity of material with one or more -CF=CH- groups. The latter lower boiling material presumably arises from decomposition of the product formed by the reverse-addition of silane to olefin as illustrated below:

$$\sim\!\!\sim\!\! CF_2CH\!=\!CH_2 \xrightarrow[H_2PtCl_6]{(CH_3)_2SiHCl} \sim\!\!\sim\!\! \underset{\overset{|}{F}}{\overset{\overset{F}{|}}{C}} - \underset{\overset{|}{SiCl(CH_3)_2}}{CH}\!-\!CH_3 \xrightarrow{\Delta} \sim\!\!\sim\!\! CF\!=\!CHCH_3$$
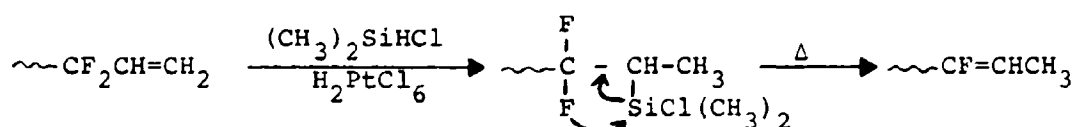
Using the above method, the following type II chlorosilanes were prepared:

Compound[*]	b.p./mm.
$(CF_2CF_2OCF_2CF_2CH_2CH_2\underset{\overset{|}{CH_3}}{\overset{\overset{CF_3}{|}\,\overset{CH_2}{|}\,\overset{CH_2}{|}}{Si}}Cl)_2$ (XIII)	137°C/.03
$(CF_2CF_2OCF_2CF_2CH_2CH_2\underset{\overset{|}{CH_3}}{\overset{\overset{CH_3}{|}}{Si}}Cl)_2$ (XIV)	88°C/.01

(continued)

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Compound*	b.p./mm.

$$CF_3$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2$$
$$|$$
$$O(CF_2CF_2CH_2CH_2\underset{|}{Si}Cl)_2 \qquad\qquad 117°C/.01$$
$$CH_3$$

(XV)

$$CH_3$$
$$|$$
$$O(CF_2CF_2CH_2CH_2\underset{|}{Si}Cl)_2 \qquad\qquad 69\text{-}72°C/.01$$
$$CH_3$$

(XVI)

* Yields are in the range of 10-20% from (I) or (VIII).

In the preparation of compounds (XIII) - (XVI), reverse-addition occurred to the extent of about 25%. It is fortunate that the reverse-addition product is so unstable that elimination occurs prior to or during distillation and the desired bis-adduct may be separated from the elimination products by distillation. Separation of the reverse-addition products would otherwise have proved difficult. Their presence as contaminants would have deleteriously affected the properties of the final polymer.

3. Bis-α,ω{4-(Diorganochlorosil}Propyloxy}Perfluoroalkylene Oxides

An alternative route to organochlorsilalkyl-substituted per-fluoroalkylene oxides which was examined briefly is outlined below.

$$O(CF_2CF_2CFO)_2 \xrightarrow{\ F^{\ominus}\ } O(CF_2CF_2CF_2O^{\ominus})_2$$

$$O(CF_2CF_2CF_2O^{\ominus})_2 \xrightarrow{\ CH_2=CHCH_2Br\ } O(CF_2CF_2CF_2OCH_2CH=CH_2)_2$$

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$$O(CF_2CF_2CF_2OCH_2CH=CH_2)_2 \xrightarrow{R_2SiHCl} O(CF_2CF_2CF_2OCH_2CH_2CH_2SiR_2Cl)_2$$
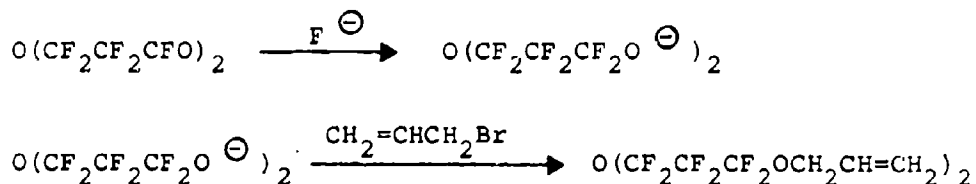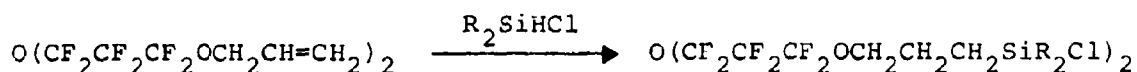
Since the key to success in this reaction sequence turns on the successful preparation of an intermediate perfluoroalkoxide, some time was spent in perfecting a reliable technique for their preparation. The carbonyl compounds which were used in this effort are $(CF_3)_2C=O$, $CF_3CF_2OCF_2CF_2CFO$, $O(CF_2CF_2CFO)_2$, $CF_2=CFOCF_2CF_2$-CFO, and $CF_3CF-C-CF_2CF_2O$.

a.   Preparation of Perfluoroalkoxides

The most satisfactory process for preparing alkoxides was found to be as follows. Cesium fluoride was weighed into a reactor which was then connected to a vacuum system. The salt was then heated with a Bunsen burner until it ceased to deflagrate, at which time it was considered to be dry. Dried diglyme or aceto-nitrile was then admitted to the reactor which was then cooled and the carbonyl compound (XS) condensed into the solvent. The re-actor was then allowed to warm to room temperature.

Formation of the alkoxide was considered to be complete when all of the solid dissolved. Excess material was then pumped out of the reactor and coreactants were added to the system.

By the above process the following salts were prepared in order to aid future identification of such species.

$$(CF_3)_2CF-\overset{\ominus}{O}-\overset{\oplus}{Cs} \qquad \text{from} \qquad (CF_3)_2C=O + CsF$$

$$CF_3CF_2OCF_2CF_2CF_2\overset{\ominus}{O}-\overset{\oplus}{Cs} \qquad \text{from} \qquad CF_3CF_2OCF_2CF_2CFO + CsF$$

$$CF_2=CFOCF_2CF_2CF_2\overset{\ominus}{O}-\overset{\oplus}{Cs} \quad \text{from} \quad CF_2=CFOCF_2CF_2CFO \quad + \quad CsF$$
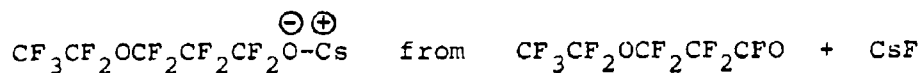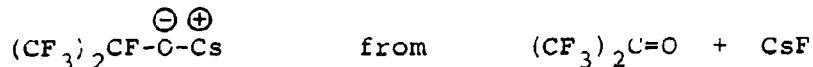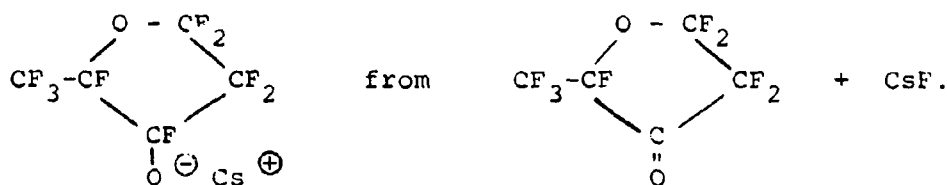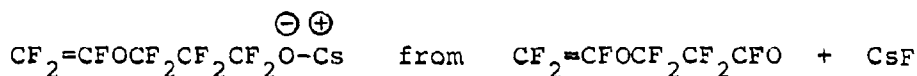
The treatment of $CF_3CF_2OCF_2CF_2CF_2\overset{\ominus}{O}-\overset{\oplus}{Cs}$ with excess $CH_2=CHCH_2Br$ gave the allyl ether $CF_3CF_2OCF_2CF_2CF_2OCH_2CH=CH_2$ in 50% yield. However, attempts to prepare the desired diene from $O(CF_2CF_2CFO)_2$ by this same procedure was not successful and this effort was terminated.

b. Reaction of $CF_2=CFOCF_2CF_2CF=O$ with Cesium Fluoride

The reaction of cesium fluoride with $CF_2=CFOCF_2CF_2CFO$ proved to be complex as a result of the competing receptor sites for attack by fluoride ion. For example, reaction of cesium fluoride with $CF_2=CFOCF_2CF_2CFO$ in the absence of solvent gave a white solid, presumably the perfluoroalkoxide. However, an attempt to reform the acid fluoride by heating the solid gave a cyclic ketone together with the starting acid fluoride and suggested that decomposition was proceeding via a carbanion intermediate (as illustrated) rather than a perfluoroalkoxide.

-16-
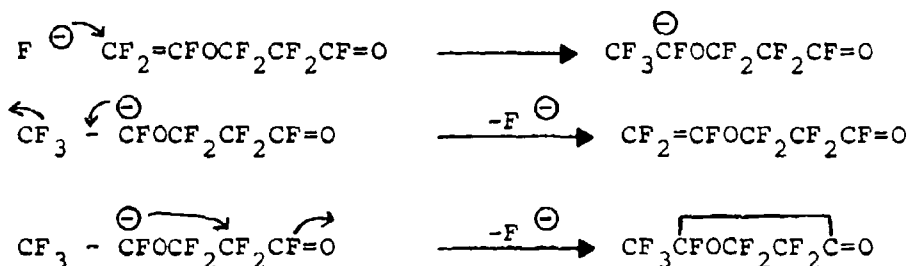
F^{19} n.m.r. spectra of the reaction between the acid fluoride and cesium fluoride in solvent (diglyme or acetonitrile) showed that the initial product is the alkoxide. Continued monitoring of the reaction by F^{19} n.m.r. showed that the alkoxide slowly reacts further as evidenced by the disappearance of the CF_2=CFO~ moiety. After all of the CF_2=CFO~ signals had disappeared the spectrum of the product was unidentifiable and did not correspond to the salt of the ketone as might have been expected.

$$
\begin{array}{ccc}
O & \!\!-\!\!\!-\!\! & CF_2 \\
| & & | \\
CF_2\text{-}CF & & CF_2 \\
& \diagdown CF \diagup & \\
& | & \\
& O \;\ominus \quad Cs \;\oplus &
\end{array}
$$
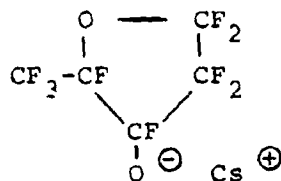
Removal of the solvent and pyrolysis of the dried solid gave the cyclic ketone together with trifluoroacetyl fluoride and not cyclic ketone and starting acid fluoride as might have been predicted from the earlier results. The effort on CF_2=CFOCF$_2$CF$_2$CFO was discontinued at this point leaving the correct reaction paths in doubt.

B.   MISCELLANEOUS SILICON COMPOUNDS

    1.   Organo-H-Chlorosilanes

        a.   Methyltrifluoropropylchlorosilane

        Synthesis of methyltrifluoropropylchlorosilane from both trifluoropropene and methyltrifluoropropyldichlorosilane was achieved by adaptation of literature reactions. The reactions used are illustrated below:

$$CF_3CH=CH_2 + CH_3SiHCl_2 \xrightarrow[175°]{H_2PtCl_6} CF_3CH_2CH_2(CH_3)SiCl_2$$

$$CF_3CH_2CH_2(CH_3)SiCl_2 \xrightarrow[\text{n-butyl ether}]{LiAlH_4} CF_3CH_2CH_2(CH_3)SiH_2$$

$$CF_3CH_2CH_2(CH_3)SiH_2 + HgCl_2 \longrightarrow CF_3CH_2CH_2(CH_3)SiHCl$$
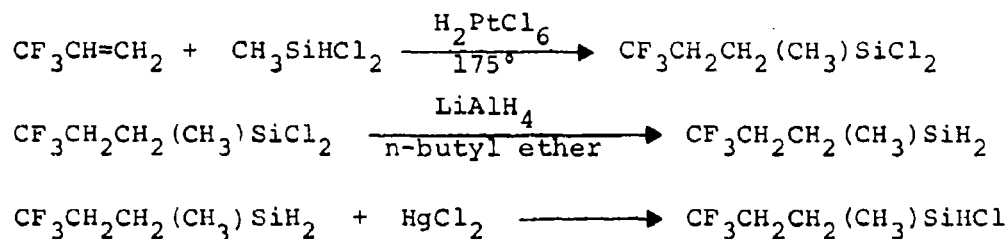
Methyltrifluoropropyldichlorosilane[7] was obtained by reaction of a 100% excess of CH_3SiHCl_2 with $CF_3CH=CH_2$ and H_2PtCl_6 catalyst in a Hastelloy bomb at 175° for 3 days. Distillation of the reaction mixture gave the dichloride, b.p. 122°, in 80-85% yield. A total of 4.53 lbs (80-83% yield) of the dichloride was prepared in this way.

Methyltrifluoropropylsilane[8] was prepared from the di-chloride by dropwise addition of the dichloride to lithium aluminum hydride in di-n-butyl ether.[9] Distillation of the unhydrolyzed reaction mixture afforded the dihydride in 90-95% yield from the dichloride, b.p. 61°.

Methyltrifluoropropylchlorosilane was first prepared by reaction of the dihydride with silver chloride and later by reaction with mercuric chloride by modification of the procedure of Anderson.[9] However, the reaction with mercuric chloride is preferred over the reaction with silver chloride as a consequence of higher yields and generally greater ease with which the re-action is accomplished.

Both reactions are carried out by adding the metal chloride to the neat dihydride in four equal portions as rapidly as the exotherm from the previous addition will allow. With silver chloride the exotherm is unpredictable, often violently exothermic and difficult to control whereas the reaction with

mercuric chloride is predictable, mildly exothermic and easily
controlled. Distillation of the reaction mixture and redistilla-
tion of the distillate affords the desired end-product in 75%
yield from mercuric chloride and 61% yield from silver chloride,
b.p. 99°. Use of a -78° gas trap in series with the reflux con-
denser during the reaction and subsequent distillation followed
by evacuation of the distillation assembly through the same gas
trap at the end of the distillation are essential to the yields
obtained.

b.   3-(Heptafluoroisopropoxy)propylmethyldichlorosilane
     and Tetrafluorocyclobutylmethyldichlorosilane

Heptafluoroisopropoxypropylmethyldichlorosilane and
tetrafluorocyclobutylmethyldichlorosilane were prepared in
anticipation of using them in place of methyltrifluoropropyldi-
chlorosilane to achieve the necessary polymer jet fuel resistance
without sacrificing thermal or hydrolytic stability.

Heptafluoroisopropoxypropylmethyldichlorosilane was
prepared by the method of Pittman[10] in 65% overall yield as
shown below:

$$(CF_3)_2C=O \ + \ KF \ \xrightarrow{\text{diglyme}} \ (CF_3)_2CFOK$$

$$(CF_3)_2CFOK \ + \ BrCH_2CH=CH_2 \ \xrightarrow[50°C]{\text{diglyme}} \ (CF_3)_2CFOCH_2CH=CH_2$$

$$(CF_3)_2CFOCH_2CH=CH_2 + \ CH_3SiHCl_2 \ \xrightarrow{H_2PtCl_6} \ (CF_3)_2CFOCH_2CH_2CH_2SiCl_2$$
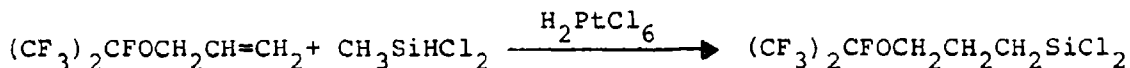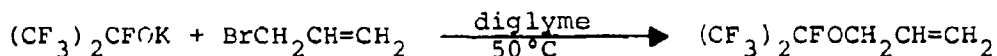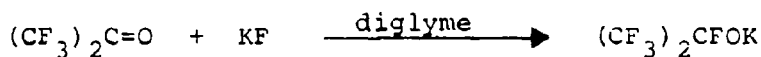
One reaction of the alkoxide and allyl bromide at 80-90°C by the
recommended procedure[10] resulted in extensive decomposition of
the alkoxide and very little of the desired product.

Although the dichloride was not converted to the mono-chloride, base hydrolysis did give the polysiloxane and no evidence of hydrolytic instability in refluxing dilute base.

Park has reported[11] that the $CF_2CF_2CH_2CHSi-$ moiety is hydrolytically stable. Hence incorporation of $CF_2CF_2CH_2CH(CH_3)-$ SiHCl into the polymers might add a measure of solvent resistance without loss of thermal or hydrolytic stability. However, hydrolysis of a sample of $CF_2CF_2CH_2CH(CH_3)SiCl_2$ with dilute sodium bicarbonate solution resulted in the formation of a yellow paste. The infrared spectrum of this material indicated that appreciable loss of fluorine had occurred and it is suspected that the normal decomposition route for silanes having fluorine on a β-carbon atom has occurred.[3]

2. Acetoxysilanes

Methyl- and heptafluoroisopropoxypropyltriacetoxysilanes were prepared by reaction of the respective trichlorosilanes with acetic anhydride at 85° for 24 hours. Distillation of the by-product acetyl chloride and then the desired triacetate afforded methyltriacetoxysilane, b.p. 98-99°/10 mm. (solidified on standing) and heptafluoroisopropoxypropyltriacetoxysilane, b.p. 116°/.07 mm., in greater than 90% yields. Vinyltriacetoxysilane was purchased from a commercial source and redistilled before using, b.p. 109°/8 mm.

C. FLUOROCARBON ETHER-BRIDGED SILOXANE POLYMERS

1. Hydrolysis of Chlorosilanes

Initially the chlorosilanes were hydrolyzed in aqueous media, either water or dilute base, and the hydrolyzates heated alone or in the presence of added sulfuric acid to effect polymer formation.

In each case, however, the polymeric product would not cure completely with triacetoxysilanes indicating that a certain quantity of inert material was present, most probably cyclosiloxanes. The results of these first polymerization reactions are presented in Table IV.

TABLE IV - Hydrolysis of

$$\begin{array}{cc} CH_3 \quad R' & R' \quad CH_3 \\ Cl\underset{\underset{CH_3}{|}}{\overset{|}{Si}}CH_2\overset{|}{C}H(CF_2CF_2OCF_2CF_2)_n\overset{|}{C}HCH_2\underset{\underset{CH_3}{|}}{\overset{|}{Si}}Cl \end{array}$$
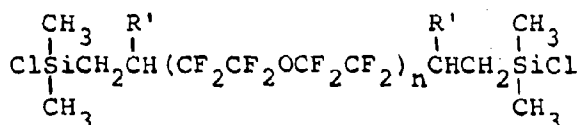
No.	Reactant R'	n	Reaction Media	Catalyst	Product $\bar{M}n$
1 a.	H	2	Ether/H_2O	-	1300
b.	hydrolyzate[a]		neat	H_2SO_4/Δ	3000
2 a.	H	1	Ether/H_2O	-	NM[c]
b.	hydrolyzate[b]		neat	Δ	5300
3 a.	H	1	H_2O/NaOH	-	NM
b.	hydrolyzate[a]		neat	H_2SO_4/Δ	6300
4 a.	CH_3	1	Ether/H_2O	-	NM
b.	hydrolyzate[b]		neat	H_2SO_4/Δ	6900
5 a.	CH_3	1	$NaHCO_3/H_2O$	-	590
b.	hydrolyzate[a]		neat	H_2SO_4/Δ	12,200
6.	CH_3	1	Water	-	7100

a) Processed hydrolyzate; b) Unprocessed hydrolyzate;
b) Not measured.

That the monomer silanols containing a central perfluorotetramethylene oxide moiety (n = 1, Table IV) will cyclize to the corresponding cyclosiloxanes in the presence of acid was shown

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by examination of the product from reaction 6 (Table IV). The
chlorosilane was hydrolyzed by adding it directly to vigorously
stirred water at room temperature. Heating the processed hydro-
lyzate ($\overline{M}n$ = 7100, f $\leqslant$0.7) $\underline{\text{in vacuo}}$ gave a small amount of dis-
tillate which was identified by boiling point and spectroscopic
analyses as the monocyclosiloxane. Despite the removal of the
monocyclosiloxane the residue could not be completely cured with
triacetoxysilanes suggesting that even higher cyclic analogs
might be present. Evidence indicating that larger rings can form
was obtained from reaction 1. There, water hydrolysis of the
silyl chloride, containing a central di-perfluorotetramethylene
oxide moiety (n = 2, Table IV),gave a hydrolyzate ($\overline{M}n$ = 1300)
which showed no OH absorption in the infrared indicating that a
certain quantity of inert material had formed, probably cyclo-
siloxanes. Heating this material in the presence of sulfuric acid
catalyst for an extended period of time increased the molecular
weight by a relatively small amount ($\overline{M}n$ = 3000), possibly by ring-
opening polymerization, but the product still showed no -OH
absorption in the infrared and would not cure completely.

In view of the apparent facility with which the silanols
from the above hydrolysis reactions cyclize, at least under acidic
conditions, literature hydrolysis and polymerization procedures
especially designed to avoid cyclization in the preparation of
silanol-ended silicon polymers were eventually adopted.[12,13]
The three-step hydrolysis procedure shown in the following equation
gave best results.

$$\underset{\overset{|}{CH_3}}{\overset{\overset{R}{|}}{Cl\,Si}}CH_2\underset{}{\overset{\overset{R'}{|}}{CH}}(CF_2CF_2OCF_2CF_2)_n\underset{}{\overset{\overset{R'}{|}}{CHCH_2}}\underset{\overset{|}{CH_3}}{\overset{\overset{R}{|}}{Si}}Cl$$

1. Aqueous NaHCO$_3$
2. Reflux
3. Devolatilize

$$HO\Big(\underset{\overset{|}{CH_3}}{\overset{\overset{R}{|}}{Si}}CH_2\underset{}{\overset{\overset{R'}{|}}{CH}}(CF_2CF_2OCF_2CF_2)_n\underset{}{\overset{\overset{R'}{|}}{CHCH_2}}\underset{\overset{|}{CH_3}}{\overset{\overset{R}{|}}{Si}}O\Big)_x H$$

-22-
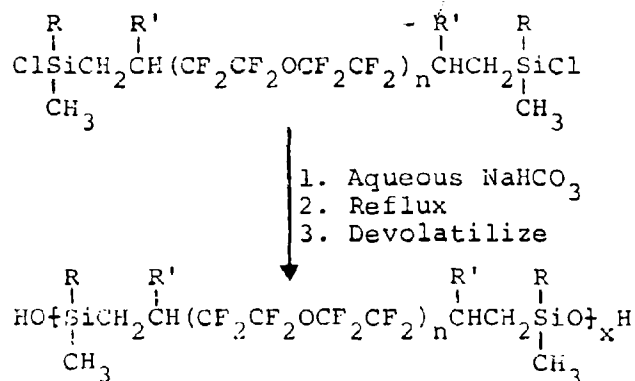
In a typical reaction, the silyl chloride was added to a slight excess of vigorously stirred saturated aqueous sodium bicarbonate solution and the mixture refluxed to condense as much monomer silanol as possible. Devolatilization of the processed hydrolyzate, typically at temperatures up to 200-250°C $\underline{in\ vacuo}$, several to remove any unreacted monomer silanol and thus precluded problems that could arise from monomer silanol cyclization in subsequent polymerization reactions. Results of several hydrolysis reactions are shown in Table V.

TABLE V - Base Hydrolysis of

$$\underset{CH_3}{\overset{R}{ClSi}}CH_2\overset{R'}{CH}(CF_2CF_2OCF_2CF_2)_n\overset{R'}{CH}CH_2\underset{CH_3}{\overset{R}{SiCl}}$$
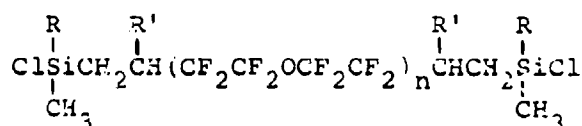
No.	Compound R	R'	n	Amt. (moles)	Reflux Period (hrs.)	Devol-atilized	Product $\overline{Mn}$	f
1 a.	CH$_3$	CH$_3$	1	.02	0[a]	no	7100	≤.7
b.				--	0	no	590	-
c.				.14	2	no	1950	1.6
d.				.34	2	no	2350	1.7
						yes	3500	1.6
2.	CH$_3$	H	1	.07	0	no	740	-
3.	CH$_3$	H	2	.02	8	no	5000	1.0
						yes	9100	1.1
4.	TFP[b]	CH$_3$	1	.14	10	no	800	2.0
5.	TFP	H	1	.13	8	no	1200	1.7

a) Water hydrolysis; b) Trifluoropropyl.

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Comparison of reactions 1 through 3 in Table V illustrates
the substantial effect both refluxing and devolatilization can
have on the molecular weight. With the trifluoropropyl deriva-
tives (reactions 4 and 5), the effect of refluxing was less
significant and suggests that these materials are somewhat less
reactive than the corresponding dimethylsilyl derivatives. In
the case of reaction 4, devolatilization turned out to be a dis-
tillation with the distillate consisting of monomer silanol,
b.p. ca. 150°C/.01 mm. (50%) and leaving a residue with a $\bar{M}n$ = 1050.

2.   Polymerization with Aqueous Sodium Bicarbonate

Several attempts were made to prepare polymer by hydrolyzing
the chlorosilanes with saturated aqueous sodium bicarbonate solu-
tion followed by heating the hydrolysis reaction mixtures for
extended periods of time. The data collected and presented in
Table VI indicate that this method may have some utility in
preparation of polymer from type II monomers (R' = H) but prob-
ably not from type I monomers (R' = CH_3).

Despite the fact that essentially identical reaction condi-
tions were used in each of the reactions presented in Table VI,
the product from reaction number 2 would not cure completely with
triacetoxysilanes. Due to the limited quantity of this type II
monomer that was prepared, repetition of this experiment was not
possible. Attempts to prepare higher molecular weight polymer
from the other type II monomers was not possible for this same
reason.

Measurement of the bulk viscosity of the product from react-
ions 2 and 3 was not possible due to insufficient material. How-
ever, these liquids appeared visually to have viscosities similar
to the polymer from the first reaction, and substantially less than
the polymers containing trifluoropropylmethyl-substituted silicon
atoms.

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TABLE VI - Hydrolysis and Polymerization of $\overset{R}{\underset{CH_3}{\underset{|}{\overset{|}{Cl\,Si}}}}CH_2CH(CF_2CF_2OCF_2CF_2)_n\overset{R'}{\overset{|}{CH}}CH_2\overset{R}{\underset{CH_3}{\underset{|}{\overset{|}{Si\,Cl}}}}$								
	Compound			Reaction[a]		Product[d]		
No.	R	R'	n	Time (hrs.)	moles	$\overline{Mn}$	f	Viscosity (cps)[c]
1.	CH_3	CH_3	1	42	.24	3200	1.4	2500
2.	CH_3	H	1	7	.034	6600	.7	–
3.	CH_3	H	2	8	.02	9100	1.1	–
4.	TFP[b]	CH_3	1	53	.14	2500	2.5	31,200
5.	TFP	H	1	48	.12	4700	2.2	27,400
6.	TFP	H	2	12	.06	12,500	1.6	22,800
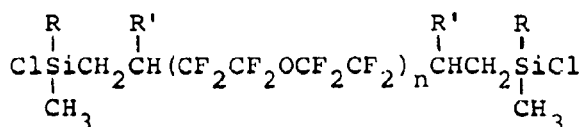
a) Reaction temperature ca. 100°C; b) Trifluoropropyl group;
c) 23-25°C; d) Devolatilized

3. Polymerization with Dilute Sodium Carbonate

Some of the early hydrolysis reactions with the trifluoro-propylmethylsilalkyl-substituted perfluorotetramethylene oxides were terminated at a point where a substantial quantity of monomer silanol was present. For this reason, reaction with aqueous sodium carbonate was carried out in an attempt to further react these monomer silanols. Three of these reactions are presented in Table VII.

The results presented in Table VII support those presented in Table VI in that the hydrolyzate from a type II monomer can be converted to polymer by heating with aqueous base while the hydrolyzate from type I monomers is more resistant to this method of polymerization.

$$HO \left(\underset{\underset{CH_3}{|}}{\overset{\overset{TFP}{|}}{Si}} CH_2 \underset{}{\overset{\overset{R'}{|}}{CH}} (CF_2CF_2OCF_2CF_2)_n CH \underset{\underset{CH_3}{|}}{\overset{\overset{R'}{|} \quad \overset{TFP}{|}}{CH_2 Si O}} \right)_x H$$
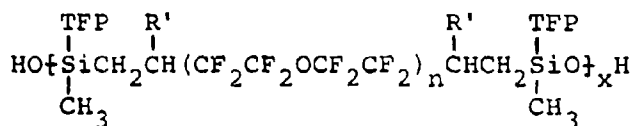
Compound			Reaction		Product	
R'	$\overline{M}n$	mole	Time (hrs)	% Base	$\overline{M}n$	f
CH_3	560	.011	104	6	1450	2.2
H	1150	.018	37	2	2150	1.6
H	1150	.054	23	7	7500	0.8

4. Polymerization with Non-Bond Rearranging Catalysts

Several catalysts that are reportedly[13] useful in the prep-
aration of the polydiorganosiloxanes were investigated as catalysts
for the polymerization of the diorganochlorosilalkyl-substituted
perfluoroalkylene oxide hydrolyzate products. Two of these, di-
butyl tin diacetate and n-hexylamine 2-ethylhexoate, gave curable
fluorocarbon ether-bridged siloxanes while the other catalysts
investigated gave products which could not be completely cured.
Data from the reactions with dibutyl tin diacetate and n-hexyl-
amine 2-ethylhexoate are presented in Table VIII.

Dibutyl tin diacetate, though an effective catalyst for the
dimethylchlorosilalkyl-substituted perfluoroalkylene oxide hydrol-
yzate of reaction 1, would not work under the same conditions
(refluxing cyclohexane) with the trifluoropropyl-containing
hydrolyzates of Table VIII. However, n-hexylamine 2-ethylhexoate
did give polymer with these compounds (reactions 2 - 5, Table
VIII).

TABLE VIII - Catalytic Polymerization of

$$HO \left(\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}} CH_2 \overset{\overset{\displaystyle R'}{|}}{C}H CF_2 CF_2 O CF_2 CF_2 \overset{\overset{\displaystyle R'}{|}}{C}H CH_2 \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}} O \right)_x H$$
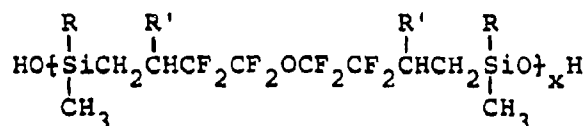
	Compound			Reaction[a]		Product	
No.	R	R'	$\overline{M}n$	Solvent	Time (hrs)	$\overline{M}n$	f
1.[b]	CH_3	CH_3	2350	cyclohexane	48	9800	2
2.	TFP	CH_3	670	neat (23°C)	16	900	–
				(120°C)	12	2900	1.5
3.	TFP	CH_3	670	benzene (23°C)	25	–	–
				reflux	24	2800	≮.3
4.	TFP	CH_3	2550	benzene	68	4700	3.3
5.	TFP	H	2150	neat (23°C)	24	–	–
				(100°C)	0.1	rubber	–

a) In refluxing solvent and n-hexylamine 2-ethylhexoate catalyst unless indicated otherwise; b) Dibutyl tin diacetate in refluxing cyclohexane.

As in the case of the base catalyzed chain extension reactions discussed previously, the hydrolyzate with the $-CH_2CH_2-$ insulating group between silicon and the perfluorocarbon ether segment, e.g., type II compounds, seems to be more reactive than the hydrolyzate with the $-CH_2CH(CH_3)-$ insulating group (compare reactions 2 and 5, Table VIII). However, development of satisfactory polymerization conditions with the type II hydrolyzate of Table VIII was not possible as a result of the limited amount of the monomer chlorosilane that was prepared.

In the presence of monomer silanol, it was found that the catalyzed polymerization of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH(CH_3)CF_2-CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$ in solvent gives some cyclosiloxane and a polymer that can only be partially cured. However, this same hydrolyzate product in the absence of solvent was converted to a curable polymer. Reactions 2 and 3 in Table VIII illustrate these points. Reaction 2 was a two-step reaction run in vacuo, first at 23°C and then continued at 120°C, to give a product that cured with a triacetoxysilane. Reaction 3, also a two-step reaction, but at atmospheric pressure and with benzene solvent, gave a product which could not be cured in the same manner, presumably because of cyclosiloxane formation. Reaction 4 was the last polymerization reaction carried out with a trifluoro-propyl-containing type I hydrolyzate product and n-hexylamine 2-ethylhexoate catalyst as a result of the termination of this contract. Based on the results of this reaction, it appears that little more than increased reaction time and/or catalyst is needed to prepare higher molecular weight, curable, silanol-ended polymer from this material.

In the early phases of the investigation, tetramethylquanidine and tetramethylquanidine di-2-ethylhexoate were examined as catalysts for the polymerization of the hydrolyzate, $HO\{(CH_3)(CF_3-CH_2CH_2)SiCH_2(CH_3)CHCF_2CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$. With these catalysts, low molecular weight hydrolyzate containing some monomer silanol was used and the reactions run in benzene solvent. In both cases, the polymer obtained ($\overline{M}n$ = 6500 and 4500) would not cure completely, and with tetramethylquanidine di-2-ethylhexoate the monocyclosiloxane was successfully isolated by distillation and identified by spectroscopic analyses. In light of reactions 2 and 3 (Table VIII) discussed above, formation of incurable polymer can probably be ascribed, in part at least, to direct cyclosiloxane formation from the hydrolyzate. However, a later attempt to polymerize the hydrolyzate of reaction

number 1 with tetramethylguanidine di-2-ethylhexoate suggests that with this catalyst another pathway to cyclosiloxane formation is possible as well. For example, a subsequent polymerization reaction using tetramethylguanidine di-2-ethylhexoate catalyst and the hydrolyzate of reaction 1 gave some monocyclosiloxane and a partially curable polymer and not a completely curable polymer as was obtained with dibutyl tin diacetate catalyst. This suggests that in addition to direct acid catalyzed cyclization of monomer silanol, the acid present is also breaking siloxane bonds and giving some monomer silanol which in turn is cyclizing to give an additional quantity of the monocyclosiloxane.

5. **Copolymerization Reactions**

   a. **Reaction of $O[CF_2CF_2C(CH_3)=CH_2]_2$ with $C_6H_5(CH_3)SiH_2$**

   An attempt was made to prepare polymer by the catalyzed reaction of $O[CF_2CF_2C(CH_3)=CH_2]_2$ with $C_6H_5(CH_3)SiH_2$ at reflux and also by heating in a sealed tube. The results indicate that this reaction is quite slow, probably slower than the reaction of $O[CF_2CF_2C(CH_3)=CH_2]_2$ with $(CH_3)_2SiHCl$, and only small quantities of polymer were obtained.

   b. **Preparation of $HO\{(CH_2=CH)(CH_3)SiO\}_x\{(CH_3)_2SiCH_2-CH(CH_3)CF_2CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_3)_2O\}_yH$**

   Two attempts were made to prepare a copolymer containing $-(CH_3)(CH_2=CH)SiO-$ and $-(CH_3)_2SiCH_2(CH_3)CHCF_2CF_2OCF_2CF_2CH(CH_3)-CH_2Si(CH_3)_2O-$ units. In the first of these, methylvinyldichlorosilane was added to an ethereal solution of $HO\{(CH_3)_2SiCH_2(CH_3)-CHCF_2CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_3)_2O\}_xH$ ($\overline{M}n = 9800$) and then triethylamine added to remove hydrogen chloride. This gave a viscous polymer which was shown to contain vinyl groups by infrared spectroscopic analysis and which was curable with diphenylsilane and platinum catalysts.

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In the second attempt, a mixture of $O[CF_2CF_2CH(CH_3)-CH_2Si(CH_3)_2Cl]_2$ (95 mole %) and $(CH_3)(CH_2=CH)SiCl_2$ (5 mole %) was hydrolyzed in saturated aqueous sodium bicarbonate solution and the mixture refluxed for 24 hours. This gave a clear polymer ($\overline{M}n$ = 3300) which clouded on standing, possibly from $HO[CH_2=CH)(CH_3)SiO]_xH$ homopolymer separating out of the fluorocarbon ether-bridged siloxane polymer. No further work was done with this material.

6. Polymer Properties

Glass transition temperature (Tg) and thermal gravimetric analysis (TGA) data on several of the fluorocarbon ether-bridged siloxane polymers is presented in Table IX. These polymers were not end-capped and the low functionalities indicate that they all contain a certain quantity of non-functional material.

TABLE IX - Properties of

$$HO\{SiCH_2\overset{R'}{C}H(CF_2CF_2OCF_2CF_2)_n\overset{R'}{C}HCH_2\overset{R}{S}iO\}_xH$$
with R, CH₃ and CH₃ substituents on the silicon atoms

No.	Compound[a]					Tg	% Wt. Loss by TGA (°C)			
	R	R'	n	$\overline{M}n$	f	(-F°)	Break	300	350	400
1.	CH₃	H	2	9,100	1.1	103	222	.5	1.5	5
2.	CH₃	H	1	6,600	.7	89	182	1	3	5
3.	CH₃	CH₃	1	5,300	.5	100	–	1	1.5	50
4.	TFP	H	2	12,500	1.6	63	162	2	4	9
5a.	TFP	H	1	4,500	.45	–	216[b]	2	6	12
b.							160	4	10	43
6.	TFP	H	1	7,500	.8	45	160	2	4	8
7a.	TFP	CH₃	1	4,500	.45	54	200[b]	3	5	11
b.							150	6	11	22

a) In air except as indicated; b) In N_2.

Due to the spread in polymer molecular weights and function-
alities, an accurate assessment of their relative thermal stabil-
ities from the TGA data is not possible. One fact that is evident
from the data is that substitution of a trifluoropropyl group for
one of the silicon methyl groups increases the Tg substantially.
This is overcome to some extent by lengthening the central per-
fluoroalkylene oxide segment as noted in sample number 4.

D. FLUOROCARBON ETHER-BRIDGED SILOXANE RUBBERS

1. Unfilled Rubber Compounds

The first successfully cured fluorocarbon ether-bridged
siloxane polymer and data collected thereon is presented in Table X.

TABLE X - Isothermal Aging and Volume Swelling of Cured

$$HO \left[\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} CH_2 \begin{array}{c} CH_3 \\ | \\ CH \end{array} CF_2 CF_2 OCF_2 CF_2 \begin{array}{c} CH_3 \\ | \\ CH \end{array} CH_2 \begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} O \right]_x H$$
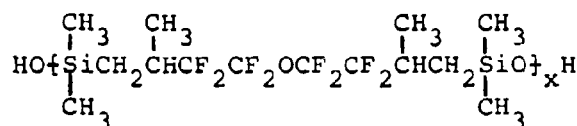
$\bar{M}n = 2350$

Sample No. [a]	Volume Swell (%) [b]	Percent Weight Loss at 350°F after 61 days	500°F after 10 days
1	dissolved	5.6	50
2	300	15.3	50
3	-	7.5	50

a) Samples 1, 2, and 3 were cured with 10%, 100%, and 200%
excesses of $(CF_3)_2 CFOCH_2 CH_2 CH_2 Si(O_2 CCH_3)_3$, respectively;
b) Jet reference fluid-30 parts toluene, 60 parts cyclohexane,
and 10 parts iso-octane.

The weight loss data indicate that the unfilled, cured poly-mer is stable in air up to 350°F for extended periods of time. Although tensile and elongation measurements were not made, manual bending and stretching of both aged and unaged specimens indica-ted that little change had taken place in the samples heat aged at 350°F. The increased weight loss of the sample cured with a 100% excess of curing agent is difficult to explain. No attempt was made to repeat the experiment.

Data on another unfilled sample, cured with three different triacetoxysilanes together with tetraisopropyl titanate curing catalyst, is presented in Table XI.

TABLE XI - Properties of Cured Samples of

$$HO\{\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}CH_2\overset{\overset{\displaystyle CH_3}{|}}{CH}CF_2CF_2OCF_2CF_2\overset{\overset{\displaystyle CH_3}{|}}{CH}CH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{Si}}O\}_xH$$
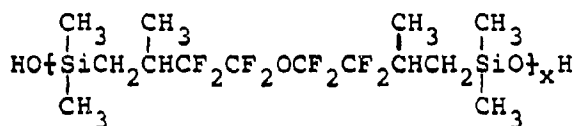
$\bar{M}n = 3500$

Triacetate	Stress (psi)	Elonga-tion (%)	Volume[a] Swell (%)	% Wt. Loss after 6 days at 500°F
$CH_2=CH-$	42	100	265 (100)[b]	47
CH_3-	60	50	220	35
$(CF_3)_2CFO(CH_2)_3-$	20	90	250	51

a) Jet reference fluid at 23°C; b) JP-4 fuel at 23°C.

The volume swelling data presented in Table XI and also Table X show that the fluorine in the polymer backbone is not sufficient to prevent excessive swelling in jet fuel. Filled polydimethyl-siloxanes have been reported[14] to swell 200% under similar con-ditions. Of the three triacetoxysilane curing agents, the methyl-substituted compound appears to be giving the more thermally

stable rubber. No attempt was made to de-gas the above samples so the tensile and elongation values may not be representative.

2. Filled Rubber Compounds

The first filled rubber compounds that were prepared and data collected thereon are presented in Table XII. In these first experiments with filled compounds, several different additives were used to enhance the strength and thermal stability of the cured samples. As with the previous samples, the additives were incorporated by hand mixing and no attempt was made to de-gas the formulations.

TABLE XII - Properties of Filled and Cured Samples of

$$HO \{ \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} CH_2 \overset{\overset{CH_3}{|}}{CH} CF_2 CF_2 OCF_2 CF_2 \overset{\overset{CH_3}{|}}{CH} CH_2 \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}} O \}_x H \qquad \overline{M}n = 9800$$
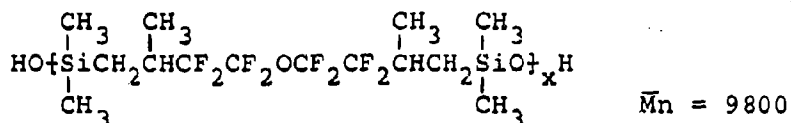
Sample No.	Stabilizer Parts	Material	Tensile (psi)	Elong- ation (%)	Volume[b] Swell (%)	% Wt. Loss[c] in Air after 50 days at 400°F		
						400°F	450°F	500°F
1[a]	-	-	315	135	100	-	-	28(6)
2[d]	70	Fe_2O_3	-	-	43	2.6	12	22
3[d]	70	$ZrSiO_4$	-	-	50	2	39(4)	45(4)
4[e]	70	Fe_2O_3	200	110	40	2.4	16	14(25)
	10	Carbon Black						

a) Filled with 23 parts of Cab-O-Sil; b) JP-4 fuel at 23°C; c) 50 days or number of days indicated in parenthesis;

d)

Ingredients	Parts by Weight
Polymer	100
Ceric hydroxide	2
Silica	7
$CH_2=CHSi(O_2CCH_3)_3$	10
Stabilizer	

e)

Ingredients	Parts by Weight
Polymer	100
Ceric hydroxide	2
$CH_2=CHSi(O_2CCH_3)_3$	10
Stabilizer	

All of the completely formulated samples (Nos. 2-4) are stable at 400°F, but lose weight at different rates above 400°F. With $ZrSiO_4$ as the thermal stabilizing additive, weight loss and embrittlement occurred very rapidly at 450°F and 500°F. With both of the iron oxide-filled samples, the rate of weight loss at 450°F and 500°F was slower and directly proportional to the number of days aged. Embrittlement was not noticeable until after 15 days of aging. Of the two iron-oxide filled samples, the one compounded with silica as the strengthening filler appears to be slightly more thermally stable.

The volume swells of the completely formulated samples are significantly improved over the Cab-O-Sil filled sample (No. 1), and lower than that reported[14] for polydimethylsiloxane. The volume changes were measured with a ruler as were the previously discussed samples and thus are approximations.

a. Volume Swell in Jet Fuel

Additional volume swelling data on filled rubber compounds is presented in Table XIII. With the exception of samples 1 and 2, these samples have been milled on a two-roll rubber mill, and deaerated by evacuating a desiccator containing the samples for 1 to 2 minutes, admitting dry air and re-evacuating. Volume swells were measured by the volume displacement method following the procedure described in ASTM-471-55D, and thus are accurate measurements. Each sample was immersed in JP-4 fuel maintained at about 23°C for at least 72 hours. Maximum swell always occurred within 24-48 hours. As shown in Table XIII, addition of a trifluoropropyl group as a side chain has reduced volume swell in JP-4 fuel to acceptable limits.

TABLE   XIII - Solvent Swelling of Cured

$$HO\{SiCH_2\overset{R}{C}H(CF_2CF_2OCF_2CF_2)_n\overset{R'}{C}HCH_2\overset{R'}{\underset{CH_3}{Si}}O\}_xH$$
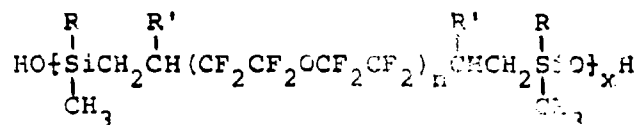
| Sample No. | Compound | | | | % Volume Swell, |
	R	R'	n	$\overline{Mn}$	JP-4 (23°C)
1[a]	CH₂	CH₃	1	9,800	70
2[b]	CH₃	H	2	9,100	30
3[c]	TFP	CH₃	1	4,700	16
4[c]	TFP	H	1	4,000	.4
5[c]	TFP	H	2	12,500	8.5
6[c]	[(CH₃)₂SiO]ₓ			60,000	248

Ingredients: (Parts per 100 parts of polymer)

a) Fe_2O_3 (70), silica (7), $CH_2=CHSi(O_2CCH_3)_3$ (10), Ce(C) (2); b) Cab-O-Sil (16), $CH_2=CHSi(O_2CCH_3)_3$ (7); c) Fe_2O_3 ( ) Cab-O-Sil (12), $CH_2=CHSi(O_2CCH_3)_3$ (8-10).

b.   Tensile Strength and Elongation

The tensile strength and elongation of several of the filled rubber compounds were measured and compared with that of a similarly formulated polydimethylsiloxane polymer (Table XIV). Part of the samples have been milled and deaerated as previously described while some have not. In either case, however, the values are quite low and suggest that higher molecular weight materials will probably be necessary for any marked improvement in strength.

TABLE XIV -   Tensile Strength and Elongation of Cured

$$HO\{SiCH_2\overset{R'}{CH}(CF_2CF_2OCF_2CF_2)_n\overset{R'}{CHCH_2}\overset{R}{SiO}\}_x H$$

(with $\overset{R}{\underset{CH_3}{Si}}$ ... $\overset{R}{\underset{CH_3}{Si}}$)
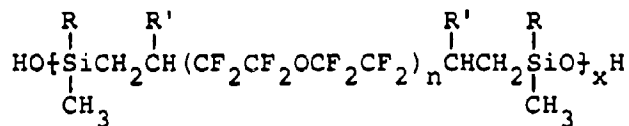
No.	R	R'	n	$\overline{M}n$	Tensile (psi)	Elongation (%)
1.	[(CH_3)_2SiO]_x			60,000	360[e]	500
2.	[b]CH_3	CH_3	1	9,800	200	110
3.	[c]CH_3	CH_3	1	9,800	330	130
4.	[d]CH_3	H	2	9,100	330	150
5.	TFP	CH_3	1	3,000	340[e]	120
6.	TFP	H	1	4,000	320[e]	60
7a.	TFP	H	2	12,500	220[e]	80
b.	Benzoyl Peroxide				220	120

a) Fe_2O_3 (5), Cab-O-Sil (12), and CH_2=CHSi(OAc)$_3$ (8-10);
b) Fe_2O_3 (70), carbon black (10), Ce(OH)$_4$ (2), CH_2=CHSi(OAc)$_3$
(10); c) Cab-O-Sil (35), CH_2=CHSi(OAc)$_3$ (5); d) Cab-O-Sil
(16), CH_2=CHSi(OAc)$_3$ (7); e) Deaerated.

c.   Thermal Analysis

Thermal analysis of each sample   consisted of thermo-
gravimetric analysis (TGA), measurement of the glass transition
temperature (Tg), and isothermal aging in air. These data are
presented in the following two tables.

TABLE XV - Thermal Analysis of Cured

$$HO \left(\underset{CH_3}{\overset{R}{\underset{|}{\overset{|}{Si}}}} CH_2 \underset{}{\overset{R'}{\underset{|}{\overset{|}{C}}}} H (CF_2 CF_2 OCF_2 CF_2)_n CH \underset{}{\overset{R'}{\underset{|}{\overset{|}{C}}}} H_2 \underset{CH_3}{\overset{R}{\underset{|}{\overset{|}{Si}}}} O \right)_x H$$
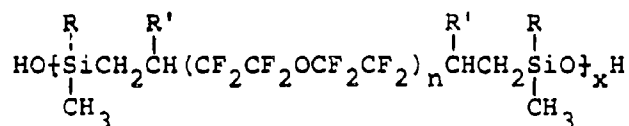
| No. | Compound | | | | Tg $(-°F)$ | % Wt.Loss by TGA[a] (°C) | | | |
	R	R'	n	$\overline{M}n$		Break	300	350	400
1[c]	CH₃	CH₃	1	9,800	98	200	1	2	3
2[c]	CH₃	H	2	9,000	101	290	0.5	1	5
3[d]	TFP	CH₃	1	3,900	36	280	0.5	2	4
4[d]	TFP	H	1	8,400	36	160	2	4	7
5[c]	TFP	H	2	12,500[b]	63	225	0.5	2	3

a) In air; b) In air and N_2; c) Formulated as given in Table XIII; d) Fe_2O_3 (30-50 parts), silica (6-20), $Ce(OH)_4$ (2), $CH_2=CHSi(OAc)_3$ (8).

From the data in Table XV, it is seen that increasing the length of the central perfluoroalkylene oxide segment has lowered the Tg of the filled rubbers, significantly in the compounds with trifluoropropyl groups on the silicon atoms (compare samples 2 and 5, and then 1, 3, and 4 with each other). Without this extra perfluoroalkylene oxide segment, the Tg's of the polymers with a trifluoropropyl group on silicon are higher than the target objective of -65°F and substantially higher than the corresponding materials with methyl groups on silicon.

TABLE XVI - Isothermal Aging in Air of Cured

$$HO \left[\begin{array}{c} R \\ | \\ SiCH_2 \\ | \\ CH_3 \end{array} \begin{array}{c} R' \\ | \\ CH \end{array} (CF_2CF_2OCF_2CF_2)_n \begin{array}{c} R' \\ | \\ CHCH_2 \end{array} \begin{array}{c} R \\ | \\ SiO \\ | \\ CH_3 \end{array} \right]_x H$$
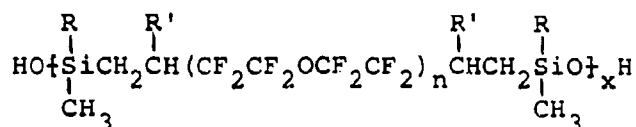
	Compound				Time	% Wt. Loss at		
No.	R	R'	n	$\bar{M}n$	(days)	400°F	450°F	500°F
1.	CH_3	CH_3	1	9,800[a]	25	2.6	7.4	12
					50	2.6	12	22
2.	CH_3	H	2	9,100[b]	3	-	-	15
3.	TFP	CH_3	1	4,700[c]	13	1.8	4	60
					50	2.6	7	-
4.	TFP	H	1	4,000[c]	15	1.8	52	56
					50	2.7	-	-
5.	TFP	H	2	12,500[c]	6	.4	1.7	61
					20	-	3.5	-
					50	2	64	-
6.	$[(CH_3)_2SiO]_x$			60,000[c]	15	1.2	2.8	3.8
					50	2.8	7	21

a) Fe_2O_3 (70), silica (7), $Ce(OH)_4$ (2), $CH_2=CHSi(OAc)_3$ (10);
b) Cab-O-Sil (16), $CH_2=CHSi(OAc)_3$ (7); c) Fe_2O_3 (5),
Cab-O-Sil (12), $CH_2=CHSi(OAc)_3$ (8-10).

The upper temperature limit of the filled rubbers was probed by means of TGA and isothermal aging in air. As with the first formulated samples discussed (page 33), these compounds exhibit good stability at 400°F, but lose weight and embrittle at different rates at higher temperatures. From the limited amount of data collected, it does appear that the compounds with a pendant methyl group on the fluorocarbon ether-bridging unit, e.g.,

type I materials, are the more stable. These materials lost weight and embrittled more slowly above 400°F than did the non-pendant methyl compounds. This includes sample number 5, which from the standpoint of molecular weight, volume swell, and Tg was potentially more valuable than either of the two pendant methyl compounds (1 .d 3) shown in Table XVI. The polydimethyl-siloxane compound was very close to the two pendant methyl compounds in terms of weight loss. However, this material remained flexible and could be twisted and bent freely after 50 days despite the weight loss shown.

d. Aging in Jet Fuel Vapor

Two of the compounds isothermally aged in air were also isothermally aged in JP-6 vapor and nitrogen at 500°F and the changes in weight, volume, tensile strength, and elongation measured over an eight-day period. Each value listed in Table XVII is the result of one measurement only.

As shown in the table, the second sample ($\overline{M}n$ = 12,500) was the better of the two having retained approximately 50% of its original tensile strength after aging for eight days. Neither sample showed any noticeable discoloration or embrittlement and was recovered from the aging vessel in its original shape.

E. FUNCTIONALLY-TERMINATED POLY (PERFLUOROALKYLENE OXIDES)

Research in the early part of this reporting period proceeded on an investigation of the poly(perfluoroalkylene oxides). This research effort was divided into two areas of interest: (1) determination of the nature of the branching reaction and the structure of the branched products obtained from the photopolymerization of perfluoroether diacid fluorides; and (2) investigation of potential curing reactions for use with functionally-terminated poly(perfluoroalkylene oxides).

The initial effort on the branching reaction was started under a related contract[2] and completed in the early stages of this contract on sealant polymers. The results from this

effort are reported in full below. Research on curing reactions
centered on efforts to prepare methyl ketone - and dihydrothiol-
terminated polymers, and on attempting to bridge the perfluoro-
alkylene oxides with aromatic amides.

1.   Branching in the Photolysis of Perfluoroether Acid
      Fluorides

The polyperfluoroethers from photolysis of perfluorooxydi-
propionyl fluoride (POPF, XVIII) and from photolysis of its
photodimer, perfluoro-4,9-dioxadodecanedioyl fluoride (POPF-D,
XIX) contain sizable quantities of branched polymer together
with linear product (see the equations below).

$$
\begin{array}{l}
O(CF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}F)_2 \\[2mm]
\qquad (XVIII) \\[6mm]
(CF_2CF_2OCF_2CF_2\overset{\overset{\displaystyle O}{\|}}{C}F)_2 \\[2mm]
\qquad (XIX)
\end{array}
\;\xrightarrow{\;h\nu\;}\;
\left\{
\begin{array}{l}
\overset{\overset{\displaystyle O}{\|}}{FC}(CF_2CF_2OCF_2CF_2)_n\overset{\overset{\displaystyle O}{\|}}{C}F \;+ \\[2mm]
\qquad n \geqq 2 \\[4mm]
\text{Branched Polymer} \;+ \\[2mm]
\overset{\overset{\displaystyle O}{\|}}{FC}F \;+\; \overset{\overset{\displaystyle OO}{\| \|}}{FCC}F \;+\; CO.
\end{array}
\right.
$$
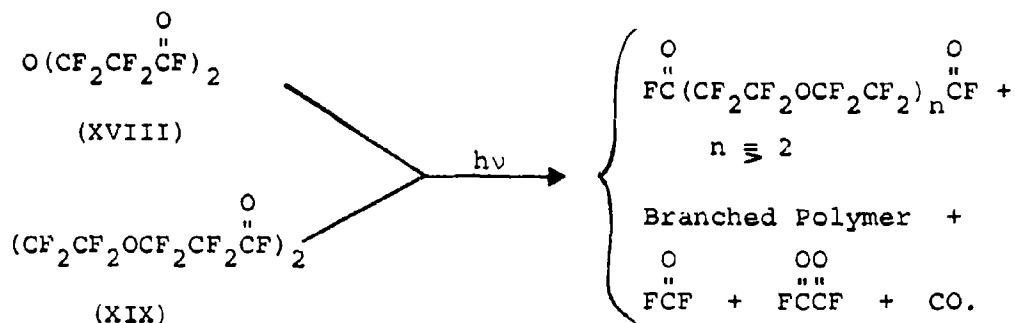
An indication of the extent of branching in the above re-
actions was obtained from an investigation made and reported in
detail under an Air Force Contract on High Temperature, High
Density Binders for Solid Propellants.[2]   However, an apprecia-
tion of the problems which generally persist in the photochemical
reactions may be obtained from a summary of the results of the
effect of reaction time on the quality of polymer from (XVIII)
and (XIX).

In summary, under the above mentioned contract the yield and number-average molecular weight ($\bar{M}n$) of the more nearly linear polymer obtained from the photolysis of POPF and POPF-D - that portion of the carboxyl-terminated polymer (obtained by hydrolyss of the acid fluoride-terminated polymer) that is soluble in Freon-113 solvent[2] - were measured as a function of reaction time. This investigation showed that the $\bar{M}n$ and yield of Freon-113 soluble polymer derived from POPF reach a maximum in about 5.5 hours ($\bar{M}n$ = 1225, f = 2.5; 38% yield). With the photodimer, POPF-D, the $\bar{M}n$ and yield reach a maximum in about 8.25 hours ($\bar{M}n$ = 1900, f = 2.5; 53% yield). Increasing the reaction time beyond 5.5 hours with POPF or 8.25 hours with POPF-D did not increase the number-average molecular weight in either case but only served to increase the yield of the branched product (Freon-113 insoluble) at the expense of the more nearly linear material.

From the above results, it was evident that a better understanding of the nature of the branching reaction and the structure of the branched products was necessary if control of the photolysis reaction and practical yields of useful photopolymer were to be obtained. The discussion that follows gives the results of further effort in this direction.

a. Background on Branching Reaction

The formation of branched products in the photolysis of fluorocarbon carbonyl-containing compounds is not without precedent. In 1962 Gordon reported[15] the formation of a branched compound (XX) in the photolysis of hexafluoroacetone and advanced the following reaction mechanism to account for its formation:

$$\text{CF}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{CF}_3 \quad \xrightarrow{\text{h}\nu} \quad 2\ \text{CF}_3\cdot + \text{CO}$$

$$2\ \text{CF}_3\cdot \quad \xrightarrow{} \quad \text{CF}_3\text{CF}_3$$

$$\text{CF}_3\overset{\overset{\text{O}}{\|}}{\text{C}}\text{CF}_3 + \text{CF}_3\cdot \quad \xrightarrow{} \quad (\text{CF}_3)_2\overset{\cdot}{\text{C}}\text{OCF}_3$$

$$(\text{CF}_3)_2\overset{\cdot}{\text{C}}\text{OCF}_3 + \text{CF}_3\cdot \quad \xrightarrow{} \quad (\text{CF}_3)_3\text{COCF}_3$$

$$(\text{XX})$$
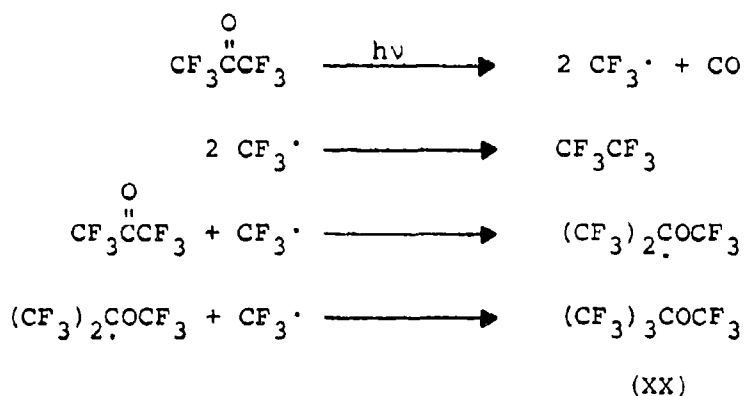
The above mechanism was later extended by Harris[16] to acid fluorides to account for the formation of a branched compound (XXI) in the photolysis of perfluorobutyryl fluoride. As indicated below, the fluoroformyl radicals either couple to form oxalyl fluoride or disproportionate to form carbonyl fluoride and carbon monoxide.

$$\text{CF}_3\text{CF}_2\text{CF}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F} \quad \xrightarrow{} \quad \text{CF}_3\text{CF}_2\text{CF}_2\cdot + \cdot\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F}$$

$$2\ \text{CF}_3\text{CF}_2\text{CF}_2\cdot \quad \xrightarrow{} \quad \text{CF}_3(\text{CF}_2)_4\text{CF}_2 \quad 58\%$$

$$\text{CF}_3\text{CF}_2\text{CF}_2\cdot + \text{CF}_3\text{CF}_2\text{CF}_2\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F} \quad \xrightarrow{} \quad \text{CF}_3\text{CF}_2\text{CF}_2\overset{\cdot}{\text{C}}\text{FOCF}_2\text{CF}_2\text{CF}_3$$

$$\text{CF}_3\text{CF}_2\text{CF}_2\overset{\cdot}{\text{C}}\text{FOCF}_2\text{CF}_2\text{CF}_3 + \text{CF}_3\text{CF}_2\text{CF}_2\cdot \xrightarrow{} (\text{CF}_3\text{CF}_2\text{CF}_2)_2\text{CFOCF}_2\text{CF}_2\text{CF}_3 \quad (10\%)$$

$$(\text{XXI})$$

$$\cdot\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F} \quad \xrightarrow{} \quad \text{F}\overset{\overset{\text{O}\ \ \text{O}}{\|\ \|}}{\text{C}}\text{CF}$$

$$\cdot\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F} \quad \xrightarrow{} \quad \text{F}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{F} + \text{CO}$$
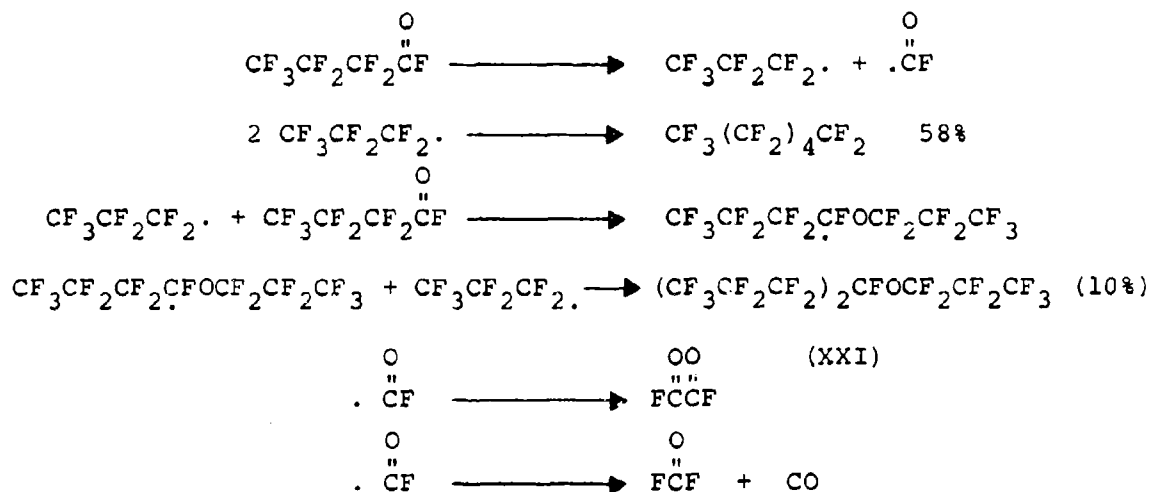
b.   Branching with Perfluoroethoxypropionyl Fluoride

Since POPF and POPF-D are difunctional, branching by the above mentioned mechanism could produce a complex mixture of

-43-

products. Because of this, the initial investigation of branching was made with a simpler perfluoroether acid fluoride, the monofunctional derivative of POPF, perfluoroethoxypropionyl fluoride.

Particular care was taken to obtain pure samples of perfluoroethoxypropionyl fluoride for the photolysis reactions. Purification was accomplished by methods similar to those previously worked out for purification of (XVIII) and are outlined in the Experimental Section.

Perfluoroethoxypropionyl fluoride was allowed to vaporize into an evacuated 500 ml quartz bulb and the gas (250 mm) irradiated with a 450 watt medium pressure lamp. Vapor phase chromatography of the reaction mixture revealed the presence of carbonyl fluoride, oxalyl fluoride, unreacted perfluoroethoxypropionyl fluoride and three higher boiling compounds. Purification by gas chromatography and characterization by the usual analytical techniques identified these new compounds as the photodimer of perfluoroethoxypropionyl fluoride (XXII), a branched acid fluoride (XXIV) and a branched perfluorinated alkyl ether (XXV). Formation of both (XXIV) and (XXV) may be rationalized by the branching mechanism previously proposed for hexafluoroacetone if one assumes that the intermediate radical (XXIII) reacts with either the fluoroformyl radical or the perfluoroethoxyethyl radical.

$$CF_3CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}F \xrightarrow{\ h\nu\ } CF_3CF_2OCF_2CF_2\cdot + \cdot\overset{O}{\overset{\|}{C}}F$$

$$2\ CF_3CF_2OCF_2CF_2\cdot \longrightarrow CF_3CF_2OCF_2CF_2CF_2CF_2OCF_2CF_3\ (60\%)$$

(XXII)

-44-

$$CF_3CF_2OCF_2CF_2 \cdot \ + \ CF_3CF_2OCF_2CF_2\overset{\overset{O}{\|}}{C}F \ \longrightarrow \ CF_3CF_2OCF_2CF_2\overset{.}{C}FOCF_2CF_2OCF_2CF_3$$

<div align="center">(XXIII)</div>

$$\overset{\overset{O}{\|}}{.C}F \qquad (XXIII) \qquad .CF_2CF_2OCF_2CF_3$$

~15%   ~25%

125 ∅   128 ∅   122 ∅   138 ∅

CF₃CF₂OCF₂$\overline{CF_2}$ $\overline{F}$ CF₃CF₂OCF₂$\overline{CF_2}$ $\overline{F}$

C   C

O=CF $\overline{OCF_2}CF_2OCF_2CF_3$ CF₃CF₂OCF₂$\overline{CF_2}$ $\overline{OCF_2}CF_2OCF_2CF_3$

-26 ∅   AB(83.6 & 92 ∅)   122 ∅   85.2 ∅

<div align="center">(XXIV)   (XXV)</div>
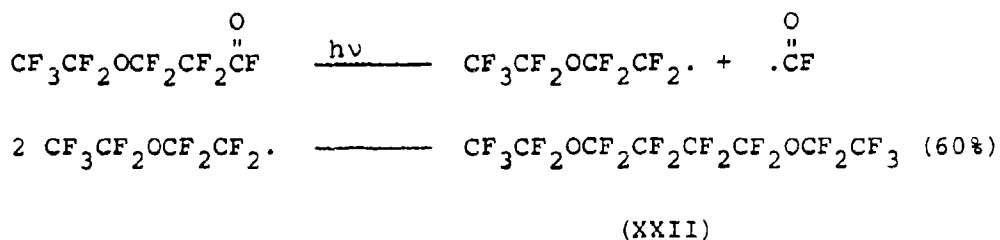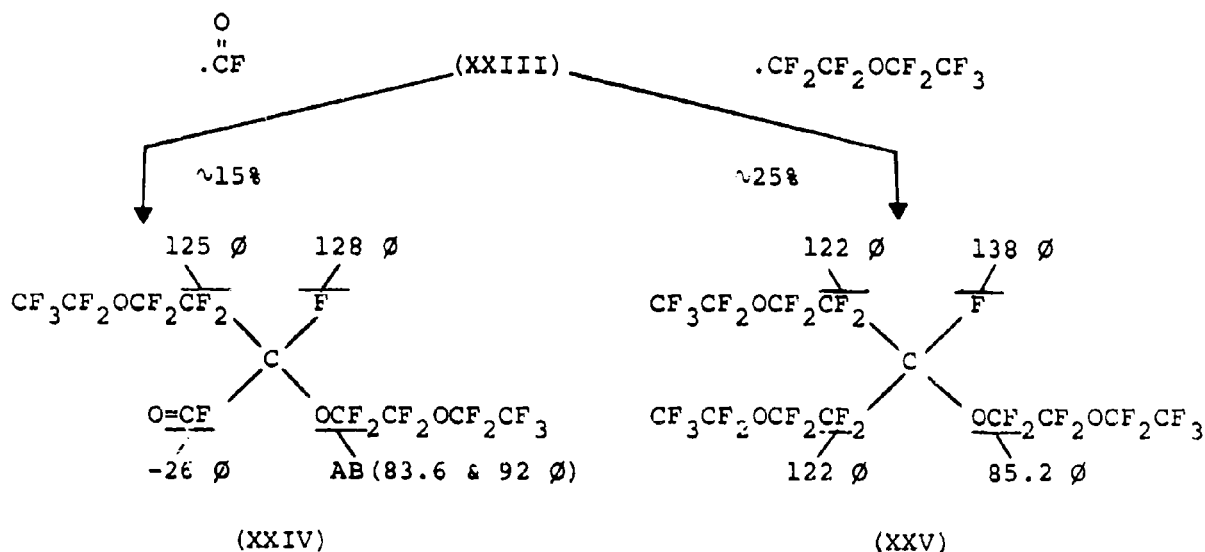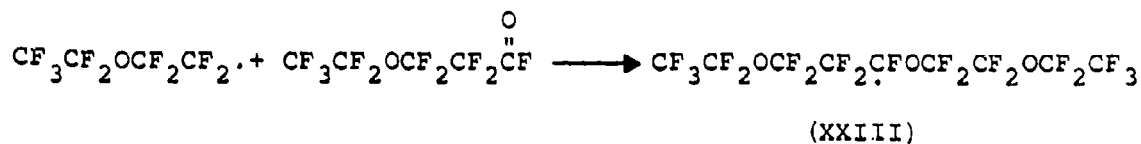
The key identifying features in the F^{19} n.m.r. spectra of (XXIV) and (XXV) are noted on the drawn structures. Assignment of a structure to the branched acid fluoride (XXIV) was greatly facilitated by the close similarity of its n.m.r. spectrum to that of a known branched acid fluoride (XXVI) previously identified as a minor constituent (4-6%) in purified (XVIII). This similarity includes an absorption for a tertiary fluorine

131 ∅   -23.5 ∅

CF₃ $\overline{F}$

C

O=CF $\overline{OCF_2}CF_2\overset{\overset{O}{\|}}{C}F$

-25.6 ∅   AB (81 & 88 ∅)

<div align="center">(XXVI)</div>

<div align="center">-45-</div>
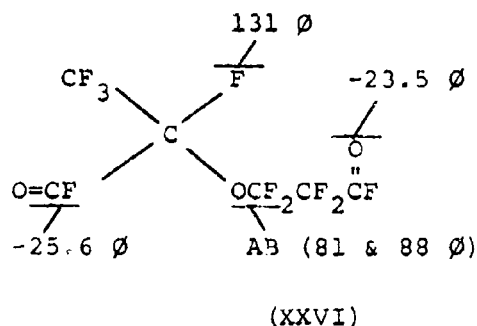
atom, an absorption for an acid fluoride group at the branch-
ing site, and an AB pattern for two fluorine atoms beta to the
branching site. Formation of (XXV) by reaction of the inter-
mediate radical (XXIII) with a perfluoroethoxyethyl radical
places two identical groups at the branching site, and thus
logically accounts for the absence of the AB pattern in (XXV)
and also accounts for the small shifts noted for the other
groups surrounding the branching site.

From the results with perfluoroethoxypropionyl
fluoride, one might expect the formation of the same kinds of
products from photolysis of perfluorooxydipropionyl fluoride
(POPF). Such products, being trifunctional, would provide
all the necessary features for formation of branched polymer.

c.   Branching with Perfluorooxydipropionyl Fluoride

The investigation of branching with POPF was made by
examining the product from the photodimerization of POPF. This
examination revealed that branched compounds analogous to those
from perfluoroethoxypropionyl fluoride are indeed formed in the
photolysis of POPF.

Photodimerization of POPF was accomplished by cycl-
ing POPF condensate through a quartz flow-through photoreactor,
collecting the higher boiling photoproducts in the boiling
flask and recycling the unreacted POPF back through the photo-
reactor.[17] The results from a typical photodimerization re-
action are shown in Table XVIII.

The product analysis in Table XVIII was arrived at by
distillation and analysis of the distillation fractions by vapor
phase chromatography. As noted, 60% of the POPF consumed was
converted to photodimer while 40% ended up in products boiling

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higher than the photodimer. Of the higher boilers, the two branched products (XXVIII and XXIX), compounds A and F in Table XVIII, were present in large amounts making up about 55% of the higher boiling fraction.

Product	Yield (g)	Yield[a] from POPF	Yield from[b] High Boilers
POPF	101	–	–
Photodimer	414	60	–
High Boilers	242	40	–
A			38
Phototrimer			9
B			3.5
C			4
D			4.5
E			4
F & Phototetramer			16
14 Misc. Peaks			16
Pot Residue			5
TOTALS		100	100

TABLE XVIII - Photodimerization of 898 g of
$O=CFCF_2CF_2OCF_2CF_2CF=O$

a) Calculated from the monomer consumed during reaction;
b) These values are equal to the percent of the denoted product in the high boiling fraction.

The photodimer of POPF (POPF-D) was readily identified by comparison with an authentic sample while the trimer, a new compound, was identified by analysis of its F^{19} n.m.r. spectrum.

This analysis included verification of the expected absorptions at 126 ∅ and 83.3 ∅ for the perfluorotetramethylene oxide repeating unit, absorptions at 86 ∅, 121.6 ∅, and -23.6 ∅ for the terminal units and measurement of the area under each absorption band.

$$\overset{O}{\overset{\|}{F}C}CF_2CF_2(OCF_2\overset{126\ ∅}{\overbrace{CF_2CF_2CF_2}})_2\overset{86\ ∅}{\overbrace{OCF_2}}CF_2\overset{O}{\overset{\|}{C}F}$$

-23.6 ∅ └─83.3 ∅─┘   121.6 ∅
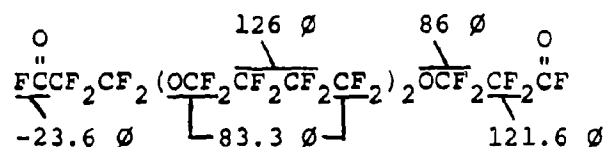
Calcd. Area Ratios - 4:4:2:2:2
Found - 3.8:3.8:1.8:1.8:1

Examination of the F^{19} n.m.r. curves of compounds A and F immediately revealed them to be complex, nonlinear structures having the same key identifying features noted earlier for the branched compounds from perfluoroethoxypropionyl fluoride. The F^{19} n.m.r. spectral analysis of A and F along with additional analytical data identified these compounds as (XXVIII) and (XXIX), respectively. Again, formation of the branched products may be rationalized by the originally proposed branching mechanism.

$$\overset{O}{\overset{\|}{F}C}CF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}F} \xrightarrow{h\upsilon} \overset{O}{\overset{\|}{F}C}CF_2CF_2OCF_2CF_2\cdot + \cdot\overset{O}{\overset{\|}{C}F}$$

$$\overset{O}{\overset{\|}{F}C}CF_2CF_2OCF_2CF_2\cdot + \overset{O}{\overset{\|}{F}C}CF_2CF_2COF_2CF_2\overset{O}{\overset{\|}{C}F} \longrightarrow \overset{O}{\overset{\|}{F}C}CF_2CF_2OCF_2CF_2CFOCF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}F}$$

(XXVII)

$$
\begin{array}{c}
\overset{O}{\overset{\|}{.C}}F \qquad\qquad \underline{(XXVII)} \qquad\qquad .CF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}F
\end{array}
$$

$$
\overset{O}{\overset{\|}{\underline{FC}}}CF_2CF_2OCF_2\underset{124\ \emptyset}{\overline{CF_2}} \qquad \underset{128\ \emptyset}{\overline{F}}
$$

-23.5 ∅

O=CF   OCF$_2\overline{CF_2}$OCF$_2$CF$_2$CF

-26.6 ∅   AB(93.3 & 91.5 ∅)

88.5 ∅

(XXVIII)

$$
\overset{O}{\overset{\|}{FC}}CF_2CF_2OCF_2\underset{122\ \emptyset}{\overline{CF_2}} \qquad \underset{138\ \emptyset}{\overline{F}}
$$

$\overset{O}{\overset{\|}{FC}}CF_2CF_2OCF_2\overline{CF_2}$ OCF$_2$CF$_2$OCF$_2$CF$_2$CF

122 ∅   85.8 ∅

(XXIX)

The key identifying features in the F^{19} n.m.r. spectra of (XXVIII) and (XXIX) are noted on the drawn structures. These include the presence of a tertiary fluorine atom in both (XXVIII) and (XXIX);an AB pattern in(XXVIII) together with an acid fluoride group which is different than those in the terminal positions; and finally, the loss of both the different acid fluoride peak and AB pattern in (XXIX) when two identical groups are placed at the branching site. Additional confirmatory evidence for the assigned structurs was obtained by decarboxylative fluorination[18] of the acids of (XXVIII) and (XXIX).

Decarboxylative fluorination of(XXIXa) gave (XXV), the same branched perfluorinated alkyl ether which was obtained from the photolysis of perfluoroethoxypropionyl fluoride. Decarboxylative fluorination of (XXVIIIa) gave (XXX) together with 20% of a material identified by F^{19} n.m.r. analysis as a mixture of (XXXI) and (XXXII). Decarboxylative fluorination experiments with the acid of POF-D also gave a similar product mixture, indicating that this reaction probably involves replacement of both CO_2H, and to a lesser degree, CF_2CO_2H.

$$\text{HO\overset{O}{\overset{\|}{C}}CF_2CF_2OCF_2CF_2}\diagdown\underset{\substack{\diagup \\ \text{HO\overset{O}{\overset{\|}{C}}} }}{\overset{\diagup F}{\underset{\diagdown OCF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}OH}{C}}} \quad \xrightarrow[F_2]{185^\circ C} \quad CF_3CF_2OCF_2CF_2CF_2OCF_2CF_2OCF_2CF_3$$

<div align="center">(XXX)</div>

$$CF_3OCF_2CF_2CF_2OCF_2CF_2OCF_2CF_3$$

<div align="center">(XXXI)</div>

<div align="center">(XXVIIIa)</div>

$$CF_3CF_2OCF_2CF_2CF_2OCF_2CF_2OCF_3$$

<div align="center">(XXXII)</div>

$$\underset{\substack{ \\ \text{HO\overset{O}{\overset{\|}{C}}CF_2CF_2OCF_2CF_2}}}{\overset{\text{HO\overset{O}{\overset{\|}{C}}CF_2CF_2OCF_2CF_2}\diagdown}{\underset{\diagup}{C}}}\overset{\diagup F}{\underset{\diagdown OCF_2CF_2OCF_2CF_2\overset{O}{\overset{\|}{C}}OH}{}} \quad \xrightarrow[F_2]{185^\circ C} \quad \underset{\substack{ \\ CF_3CF_2OCF_2CF_2}}{\overset{CF_3CF_2OCF_2CF_2\diagdown}{\underset{\diagup}{C}}}\overset{\diagup F}{\underset{\diagdown OCF_2CF_2OCF_2CF_3}{}} \quad +$$

<div align="center">(XXIXa)   (XXV)</div>

<div align="center">unidentified products</div>

$$\text{HO\overset{O}{\overset{\|}{C}}CF_2CF_2O(CF_2)_4OCF_2CF_2\overset{O}{\overset{\|}{C}}OH} \quad \xrightarrow[F_2]{185^\circ C} \quad CF_3CF_2OCF_2CF_2CF_2CF_2OCF_2CF_3 \quad +$$

<div align="center">(XXII)</div>

$$CF_3OCF_2CF_2CF_2CF_2OCF_2CF_3$$

<div align="center">(XXXIII)</div>

Finally, an investigation of branching in the photo-
polymerization of POPF was made by examining the product from a
2.5 hour photopolymerization reaction of POPF in FC-75. Dis-
tillation of the reaction mixture gave, after separation of the
FC-75 and unreacted POPF (6.7 g), the distilled products shown
in Table XIX (3.8 g) together with a residue (8.6 g) with a $\bar{M}n$
of 1000 and functionality of 2.6.

<div align="center">-50-</div>

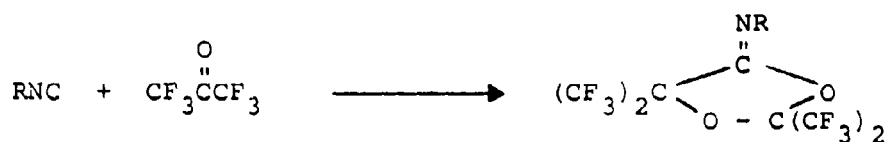TABLE XIX - Distillate from Photo-
polymerization of POPF

Compound	% Yield
Photodimer	25
(XXVIII) A	12
Phototrimer	36
(XXIX) F	7
4 unknowns	10

The formation of the branched products (XXVIII) and
(XXIX) in the polymerization reaction in relatively large amounts
compared to other possible branched compounds (4 unknowns) leaves
little doubt that the major branching reaction with POPF is
occurring via the reaction scheme discussed earlier. This is
also supported by the fact that <u>all</u> of the F^{19} n.m.r. spectra
of polymer from POPF appear as if they were mixtures of the
branched compounds (XXVIII) and (XXIX) and linear multiples of
POPF.

No attempt was made to isolate and identify branched
compounds from photopolymerization of POPF-D. However, the fact
that all of the F^{19} n.m.r. spectra of polymer from this diacid
fluoride have the same absorptions as the spectra of polymer
from POPF indicates that the same branching reactions occur dur-
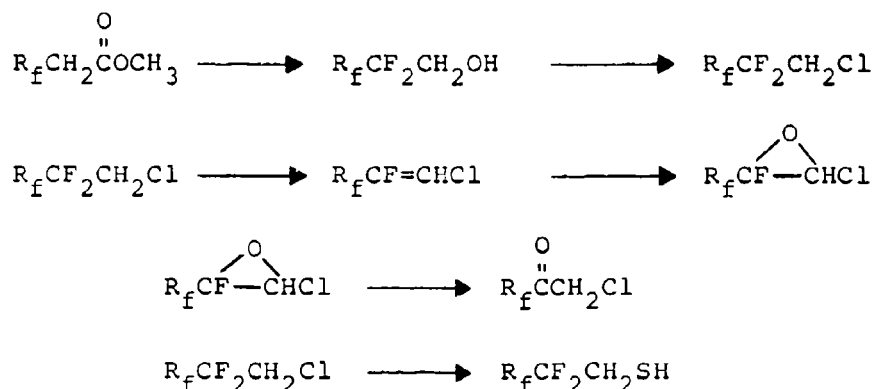ing photopolymerization of POPF-D.

2.   <u>Preparation of Ketone- and Dihydrothiol-Terminated</u>
     <u>Polymer</u>

Interest in ketone-terminated polymer rested on literature
reports[19] that hexafluoroacetone and isonitriles react to give
thermally (300°C), and acid and base stable iminodioxolanes:

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$$RNC \ + \ CF_3\overset{\overset{\displaystyle O}{\|}}{C}CF_3 \ \longrightarrow \ (CF_3)_2C\underset{O \ - \ C(CF_3)_2}{\overset{\overset{\displaystyle NR}{\overset{\|}{C}}}{\diagup\diagdown}}O$$

Work under another contract[2] had shown that methyl ketones and isonitriles do give reasonably stable polymers while isopropyl ketones do not react, apparently because of steric hindrance.

The synthetic route chosen for the preparation of the methyl ketone and dihydrothiol-terminated polymers is outlined below.

$$R_fCH_2\overset{\overset{\displaystyle O}{\|}}{C}OCH_3 \ \longrightarrow \ R_fCF_2CH_2OH \ \longrightarrow \ R_fCF_2CH_2Cl$$

$$R_fCF_2CH_2Cl \ \longrightarrow \ R_fCF=CHCl \ \longrightarrow \ R_f\overset{\overset{\displaystyle O}{\diagup\diagdown}}{CF-CHCl}$$

$$R_f\overset{\overset{\displaystyle O}{\diagup\diagdown}}{CF-CHCl} \ \longrightarrow \ R_f\overset{\overset{\displaystyle O}{\|}}{C}CH_2Cl$$

$$R_fCF_2CH_2Cl \ \longrightarrow \ R_fCF_2CH_2SH$$

Attempts to convert the model compound, $CF_3(CF_2)_6CH_2OH$, to the chloride by reaction with thionyl chloride gave instead a mixture of the corresponding sulfonyl chloride and sulfite ester.

$$CF_2(CF_2)_6CH_2OH + SOCl_2 \longrightarrow CF_3(CF_2)_6CH_2SO_2Cl + [CF_3(CF_2)_6CH_2O]_2SO$$
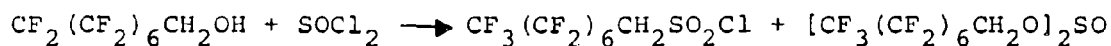
Alternate methods of preparation of the chloride have not been attempted. Possibly the difficulty with thionyl chloride could e circumvented by reaction of the acid fluoride-terminated polymers with olefins as shown below.

$$R_f\overset{\overset{\text{O}}{\|}}{C}F \;+\; CF_2{=}CF_2 \;\longrightarrow\; R_f\overset{\overset{\text{O}}{\|}}{C}CF_2CF_3$$

Attempts to form the iminodioxolanes by rea..ion of an acid fluoride and chloride with isonitriles have given what appears to be the α-addition product and not the hoped for iminodik.xolane.

$$R_f\overset{\overset{\text{O}}{\|}}{C}X \;+\; CNR \;\longrightarrow\; R_f\overset{\overset{\text{O}}{\|}}{C}CX \cdots$$

3. Preparation of Aromatic Amide Linked Polymer

Work on preparation of aromatic amide linked polymers was limited to preparation of the N-methylanilide of an ester-terminated poly(perfluorotetramethylene oxide) sample ($\overline{M}n$ = 1800, f = 2.8). The reaction of the ester and N-methylaniline was carried out in trifluoroethanol solvent. Heat aging of the product at 350°F resulted in extensive decomposition and embrittlement of the sample within 48 hours.
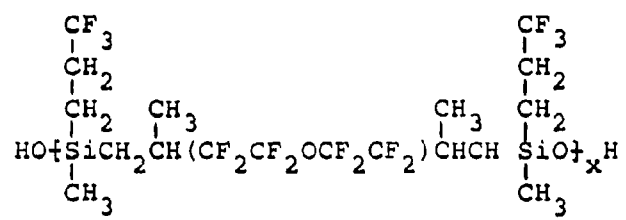
III. CONCLUSIONS AND RECOMMENDATIONS

The photolysis of perfluorooxydipropionyl fluoride (XVIII) and its photodimer results in the formation of a sizable quantity of branched polymer with a functionality greater than three. Although the more nearly linear polymer which is desired for sealant applications may be separated from the more highly branched material by extracting it from the bulk polymer with Freon-113, neither the yield nor the molecular weight of the extracted polymer is high.

On the other hand, the diorganochlorosilalkyl-substituted perfluoroalkylene oxides may be chain-extended to give high yields of linear polymer by proper choice of reaction conditions. Although more data relating polymer molecular weight to reaction time and temperature and to catalyst concentration is desirable, branching does not occur and obtainment of high molecular weight polymer is possible.

Sealant compounds prepared from the fluorocarbon ether-bridged siloxane polymers, iron oxide and silica filler, and vinyl triacetoxysilane curing agent have shown long-term stability in air up to 400°F and short-term stability up to 500°F in air and in JP-6 vapor and nitrogen. However, investigation of additional fillers and curing systems as well as variations in polymer molecular weight is needed to establish the upper temperature performance limit.

Considering the overall results of this research, the polymer species shown below appears to have the greatest potential for achieving the contract target objectives for a high-temperature integral fuel tank sealant material.

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$$\text{HO}\!\!-\!\!\left(\!\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{\overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{|}}}}\!\!Si\!-\!CH_2\!-\!\underset{\displaystyle CH_3}{\overset{|}{CH}}(CF_2CF_2OCF_2CF_2)\underset{\displaystyle CH_3}{\overset{|}{CH}}\!-\!CH\!-\!\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CF_3}{|}}{\overset{\displaystyle CH_2}{\underset{\displaystyle CH_2}{|}}}}\!\!Si\!-\!O\!\right)_{\!x}\!\!H$$

IV. EXPERIMENTAL

The data collected on the fluorocarbon ether-bridged siloxane polymers and the rubbers derived therefrom are presented in the discussion. Nuclear magnetic resonance data notations used here are: singlet (s); doublet (d); multiplet (m); complex (c); broad (b); and very broad (vb).

A. FLUOROCARBON ETHER-BRIDGED CHLOROSILANES

1.   ·-α,ω-{2-{Diorganochlorosil}-1-Methylethyl}Perfluoroalkylene Oxides

a.   Preparation of $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)(CH_2CH_2CF_3)-Cl]_2$ (VI)

(1) $O[CF_2CF_2C(CH_3)_2OH]_2$

A solution of methyl magnesium iodide in diethyl ether (1000 ml) was prepared from methyl iodide (4.4 moles) and magnesium turnings (4.4 g - atoms) in the conventional manner. A solution of $O[CF_2CF_2CO_2CH_3]_2$ (1.0 mole) in an equal volume of diethyl ether was added to the methyl magnesium iodide at a rate sufficient to maintain rapid reflux of the ether. After the addition was completed the resulting reaction mixture was refluxed for two hours. The cooled reaction mixture was poured onto cracked ice and acidified with 12N HCl and the $O[CF_2CF_2C(CH_3)_2OH]_2$ product isolated by extraction. The alcohol is a white solid at room temperature and has a boiling point of 75°C/0.3 mm.

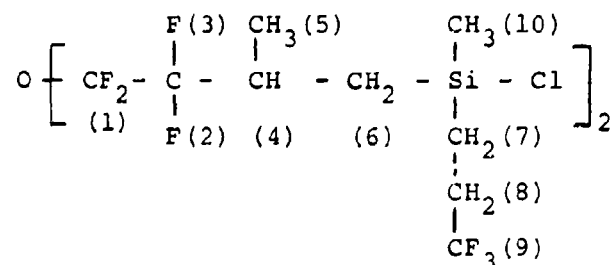(2) $O[CF_2CF_2C(CH_3)=CH_2]_2$ (II)

A mixture of the alcohol from above and 750 ml of 36N sulfuric acid was heated to 165°C over a 2-3 hour period. The desired olefin formed a layer on top of the acid and was isolated

by means of a separatory funnel. Distillation gave pure (II),
b.p. 157°C/atm. press., in 81% overall yield from (I):ir (neat)
6.0 μ (C=C); ^{19}F and ^{1}H nmr, ∅* 86.9 (O$\underset{\sim}{C}$F$_2$), 117.7 (OCF$_2\underset{\sim}{C}$F$_2$),
τ 8.09 (CH$_3$, slightly broadened), 4.42 and 4.54 (=$\underset{\sim}{C}$H$_2$, AB type
pattern with some evidence of coupling to fluorine or to the
methyl group).

In a separate experiment, crude tert-alcohol was con-
verted to the acetate ester by refluxing with excess acetyl
chloride overnight. The excess acetyl chloride was then removed
by evaporation and the ester pyrolyzed at 570°C at an addition
rate of 12-15 g/hr and N$_2$ purge rate of ca. 25 ml/min. The over-
all yield of distilled (II) from I was 55%.

(3). Addition of CF$_3$CH$_2$CH$_2$(CH$_3$)SiHCl to (II)

A mixture of (II)(0.22 mole), CF$_3$CH$_2$CH$_2$(CH$_3$)SiHCl (0.66
mole), and H$_2$PtCl$_6$ catalyst was placed in a Hastelloy bomb under
nitrogen, the bomb sealed and then heated with shaking at 150°C
for 7 days. Distillation of the reaction mixture gave (VI) (67%
yield), b.p. 119°C/.01 mm. The nmr spectra was in agreement with
the assigned structure and had the following absorptions:

$$
O\left[CF_2- \underset{\underset{F(2)}{|}}{\overset{\overset{F(3)}{|}}{C}} - \underset{(4)}{CH} - \underset{(6)}{CH_2} - \underset{\underset{CH_2(7)}{|}}{\overset{\overset{CH_3(10)}{|}}{Si}} - Cl \right]_2
$$

(1)   (4)   (6)

CH$_2$(8)

CF$_3$(9)

(1) 83.6 ∅*; (2) 118.3 ∅*, half of an AB pattern with J$_{AB}$ = 265
c/s; (3) 124.4 ∅*, other half of AB pattern, J$_{AB}$ = 265 c/s; (4) ca.
7.50 τ; (5) 8.89 τ (d); (6) and (7) complex AB types, overlapping
with other absorptions and an accurate chemical shift assignment
is not possible; (8) ca. 7.85 τ; (9) 69.3 ∅* (t); (10) 9.53 τ (s).

Anal. Calcd. for $C_{18}H_{26}Cl_2F_{14}OSi_2$: C, 33.18; H, 4.02; Cl, 10.88; F, 40.83. Found: C, 33.3; H, 3.9; Cl, 10.8; F, 40.7.

A lower boiling fraction is always obtained from this reaction, b.p. 67-69°C/.01 mm. Spectroscopic analyses and analogy with the addition of $(CH_3)_2SiHCl$ to $O[CF_2CF_2C(CH_3)=CH_2]_2$ as described below indicate that this compound is the product arising from incomplete reaction of $CF_3CH_2CH_2(CH_3)SiHCl$ with (II). ^{19}F and
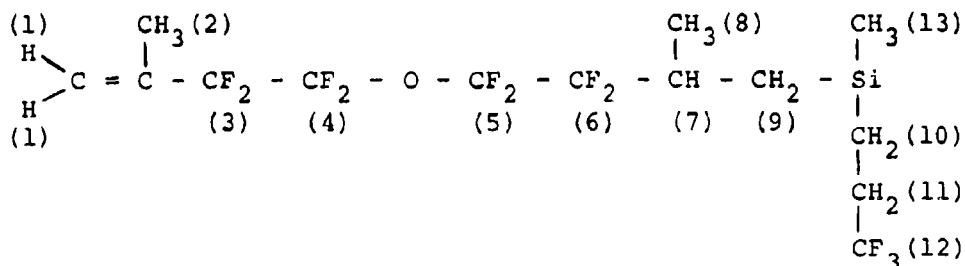
^1H nmr spectra: (1) τ 4.42 and 4.54; (2) 8.06; (3) ∅* 117.5; (4) 86.8; (5) 84; (6) 119 and 125 (AB); (7) τ 7.5; (8) 8.77; (9) and (10) 8.8; (11) 7.8; (12) 69.5 ∅*; (13) 9.51 τ.

b. Preparation of $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$ (IV)

Using the procedure of example 1(3). above, (II)(0.34 mole) was reacted with $(CH_3)_2SiHCl$ (1.34 mole) at 15ᶜ°C for 11 days. Distillation gave (IV), 81% yield, b.p.   90°C/.03 mm. ^{19}F and ^1H nmr spectra: (1) 83.7 ∅*; (2) 118.7 ∅*, half of an AB
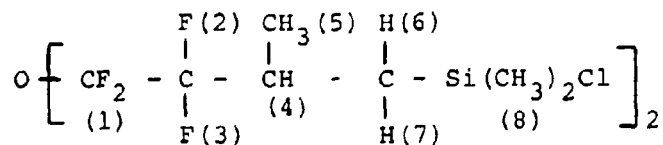
pattern with J_{AB} = 265 c/s (d, J = 11.8 c/s); there is also further doubling due to isomers; (3) 124.4 ∅*, other half of AB (d, J = 16.5 c/s); (4) 7.55 τ (vb); (5) 8.79 τ (d, J = 6.7 c/s); (6) 8.7 τ,

half of an AB with J_{AB} = 15.2 c/s (d, J = 2.5 c/s); (7) 9.1 τ, other half of AB (d, J = 10.0 c/s); (8) 9.54 τ (s).

Anal. Calcd. for $C_{14}H_{24}Cl_2F_8OSi_2$: C, 34.50; H, 4.96; F, 31.18. Found: C, 34.6; H, 4.9; F, 31.4.

As in the reaction of $CF_3CH_2CH_2(CH_3)SiHCl$ with (II), reaction of $(CH_3)_2SiHCl$ with (II) gave a lower boiling product, ca. 55°C/.03 mm which has been identified as the product from incomplete reaction of the silane with the olefin: ^{19}F and ^1H nmr:
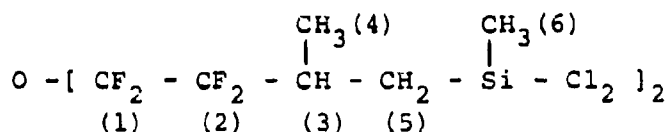
$$CH_2=C-CF_2-CF_2-O-CF_2-\underset{\underset{F(6)}{|}}{\overset{\overset{F(7)}{|}}{C}} - \underset{(8)}{CH} - \underset{\underset{H(11)\ (12)}{|}}{\overset{\overset{CH_3(9)\ H(10)}{|\qquad|}}{C-Si-(CH_3)_2Cl}}$$

with labels CH₃(2) on C, (1)(3)(4)(5) underneath.
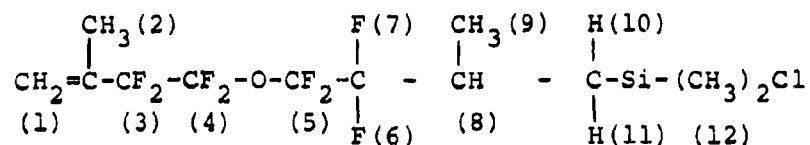
(1) 4.42 and 4.56 τ (c); (2) 8.09 τ; (3) 117.6 ø*; (4) 86.8 ø*; (5) 83.8 ø*; (6) 118.8 ø*, half of an AB pattern with J_{AB} = 264 c/s (d, J = 13.1 c/s); (7) 124.6 ø*, other half of AB pattern (d, J = 16.4 c/s); (8) 7.53 τ (vb); (9) 8.82 τ (d, J = 6.6 c/s); (10) ca. 8.7 τ, half of an AB pattern with J_{AB} = 15.7 c/s (d, J = 2.7 c/s); (11) 9.1 τ, other half of AB (d, J = 10.7 c/s); (12) 9.56 τ.

Anal. Calcd. for $C_{12}H_{15}ClF_8OSi$: C, 36.88; H, 3.87; F, 38.90. Found: C, 36.7; H, 4.4; F, 38.4.

c. Preparation of $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)Cl_2]_2$ (VII)

Using the procedure of example 1(3), (II) (0.11 mole) was reacted with CH_3SiHCl_2 (0.44 mole) at 150°C for 11 days. Distillation of the reaction mixture gave (VII), b.p. 93-98°C/.02 - .03 mm, in 88% yield. A center cut was used for analyses: ^{19}F and ^1H nmr, (1) ø* 83.7; (2) 118.1 and 124.6 (AB pattern with structure, J_{AB} = 266 cps, fine detail shows an extra doublet which is probably
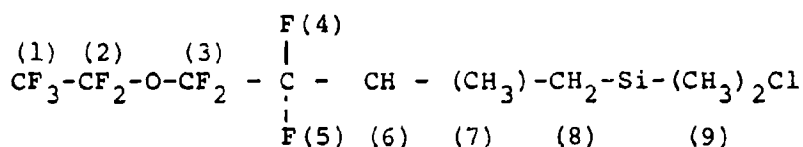
$$O - [CF_2 - CF_2 - \overset{\overset{\displaystyle CH_3 \, (4)}{|}}{CH} - CH_2 - \overset{\overset{\displaystyle CH_3 \, (6)}{|}}{Si} - Cl_2]_2$$
$$ (1) \quad\; (2) \quad\;\; (3) \quad\; (5)$$

due to isomer); (3) τ 7.42 (b and c); (4) 8.72 (d); (5) 8.42 and 8.83 (AB with $J_{AB} \simeq$ 15 cps, also additional doubling is evident); (6) 9.19.

Anal. Calcd. for $C_{12}H_{14}Cl_4F_8OSi_2$: C, 27.28; H, 3.44; Cl, 26.85; F, 28.77. Found: C, 27.2; H, 3.5; Cl, 26.6; F, 28.4.

d. Preparation of $CF_3CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl$
(III)

This compound was prepared by reaction of $(CH_3)_2SiHCl$ with $CF_3CF_2OCF_2CF_2C(CH_3)=CH_2{}^{(1)}$ at 150°C in a sealed ampoule, b.p. 164°C/atm. press. ^{19}F and ^1H nmr: (1) 87.6 ∅*; (2) 89.1 ∅*;

$$\underset{\displaystyle (1) \;\; (2) \quad\;\; (3)}{CF_3 - CF_2 - O - CF_2} - \overset{\overset{\displaystyle F\,(4)}{|}}{\underset{\underset{\displaystyle F\,(5)}{|}}{C}} - \underset{(6)}{CH} - \underset{(7)}{(CH_3)} - \underset{(8)}{CH_2} - Si - \underset{(9)}{(CH_3)_2Cl}$$

(3) 83.4 ∅*; (4) 118.8 ∅* (c, J = 12.7 c/s); (5) 124.6 ∅* (d, J = 16.1 c/s); (6) 7.53 τ (c); (7) 8.78 τ (d, J = 6.0 c/s); (8) 8.7 τ and 9.1 τ (AB with J = 15.4 c/s); (9) 9.55 τ (s).

Anal. Calcd. for $C_9H_{12}ClF_9OSi$: C, 29.1; H, 3.74; F, 46.1. Found: C, 29.3; H, 3.4; F, 45.5.

2. Bis-α,ω{2-(Diorganochlorosil)-Ethyl}Perfluoroalkylene Oxides

a. Preparation of $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)(CH_2CH_2CF_3) - Cl]_2$ (XIII)

(1) $[CF_2CF_2OCF_2CF_2CH(O_2CCH_3)CH_3]_2$ (IX)

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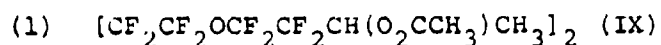
A mixture of methyl magnesium iodide and isopropyl magnesium bromide in diethyl ether was prepared from methyl iodide (0.4 mole) and isopropyl bromide (0.56 mole) and magnesium turnings (0.96 g-atom) in the conventional manner. A solution of $[CF_2CF_2-OCF_2CF_2CO_2CH_3]_2$ (0.19 mole) in an equal volume of diethyl ether was added to the mixture of organometallics at a rate sufficient to maintain a rapid reflux of the ether. After the addition was completed the reaction mixture was refluxed for 2 hours. The cooled reaction mixture was then poured onto crushed ice and acidified with 12N HCl and $[CF_2CF_2OCF_2CF_2CH(OH)CH_3]_2$ isolated by extraction. Distillation gave the alcohol as an impure, clear, colorless liquid, b.p. 74-78°C/.01 mm, (74% yield): ir (neat) 2.95 μ (OH), ^{19}F and ^1H nmr: 6.25 τ (OH, b), 5.83 τ (CH, vb), 8.63 τ (CH$_3$, d), 126.60 φ* and 131.2 φ* (CHC$\underset{\sim}{F}_2$, J_{AB} 273 c/s), 84.0 φ* (CHCF$_2$C$\underset{\sim}{F}_2$O, b and run together), 126.0 φ* (OCF$_2$C$\underset{\sim}{F}_2$C$\underset{\sim}{F}_2$CF$_2$O, b), 83.0 φ* (OC$\underset{\sim}{F}_2$-CF$_2$CF$_2$C$\underset{\sim}{F}_2$O, c).

Reaction of the alcohol with excess acetyl chloride at room temperature overnight and at 70°C for 2 hours gave (IX), b.p. 94-97°C/.75 mm, in ca. 50% yield from (VIII) of about 85% purity by VPC, with four impurities making up 15% of the fraction. A center cut was used for analyses and showed: 5.6 μ (C=O); nmr: 7.96 τ (C$\underset{\sim}{H}_3$CO, s); 4.58 τ (CH, double-5 fold coupled to CH$_3$ with J = 6.6 c/s, and to one F atom with J = 8.2 c/s, and to the second adjacent F atom with J = 15.6 c/s); 8.61 τ (CH$_3$, d); 122.2 φ* and 129.7 φ* (CHC$\underset{\sim}{F}_2$, J_{AB} 276 c/s); 84.6 φ* (OC$\underset{\sim}{F}_2$CF$_2$CH, c); 83.4 φ* (OC$\underset{\sim}{F}_2$CF$_2$CF$_2$C$\underset{\sim}{F}_2$O, c); 125.8 φ* (OCF$_2$C$\underset{\sim}{F}_2$C$\underset{\sim}{F}_2$CF$_2$O, m).

Anal. Calcd. for $C_{16}H_{14}F_{16}O_6$ (606.27): C, 31.70; F, 50.14; H, 2.33. Found: C, 31.9; F, 49.8; H, 2.3.

(2) Preparation of $[CF_2CF_2OCF_2CF_2CH=CH_2]_2$ (X)

Formation of (X) from (IX) was effected by dropping the latter compound onto a 32 cm heated section of small quartz tubes

(3 mm x 10 mm) packed into a vertical quartz tube 2.8 cm in diameter and 60 cm in total length. Preliminary experiments with $O[CF_2CF_2CH(O_2CCH_3)CH_3]_2$ and $CF_3(CF_2)_6CH(O_2CCH_3)CH_3$ as described in subsequent sections pointed toward the 500+ °C range for pyrolysis of (IX). Preliminary small scale experiments with (IX) itself indicated that satisfactory yields of diene could be obtained by pyrolysis at 570°C in conjunction with a nitrogen purge rate of 10 ml/min. and an acetate addition rate of ca. 15 g/hr. The results of these experiments culminating in pyrolyses at 570°C are shown in the table below.

Pyrolysis of $[CF_2CF_2OCF_2CF_2CH(O_2CCH_3)CH_3]_2$

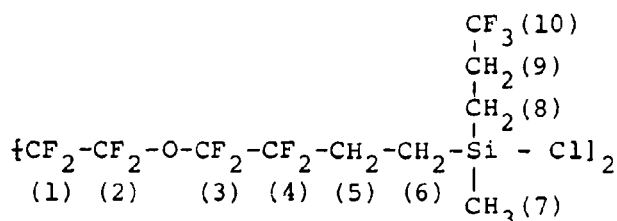| Reaction			Products[a] (%)			
Amt.	t, °C	N_2 (cc/min)	Wt. Pyrolyzate	Diene	Half Pyrolyzed	Unreacted
(g)			(g)			
2	535	10	1.7	70	26	4
2	550	10	1.6	82	16	2
2	550	25	1.6	92	10	0
1.8	570	10	1.4	98	2	0
30[b]	570	10	28.4	82	15[c]	2[c]

a) Percentages are from VPC area measurements on diene, half-pyrolyzed and unreacted ester; b) added over 2.25 hrs.; c) re-pyrolysis gave a 75% yield of isolable diene from this reaction.

As noted in the table, 75% yields of pure diene can be obtained by repyrolysis of unreacted material. Generally, this was not done. In a typical reaction, 0.21 mole of (IX) was pyrolyzed at 570°C and the olefin isolated in 50% yield (VPC analysis) by washing the crude pyrolyzate product with water and then distilling the dried product through a Podbelniak packed distillation column and

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taking the two center cuts for subsequent reactions : cut 1, b.p. 74-77°C/14 mm, 95% pure by VPC; cut 2, b.p. 77-80°C/14 mm, 88% pure by VPC. A sample for analysis was obtained by redistillation, b.p. 75°C/13 mm. ^{19}F and ^{1}H nmr: 4.15 τ ($\underline{CH}_2$=$\underline{CH}$, c); 118.5 ∅* (=CH-$\underline{CF}_2$, c); 88.3 ∅* (CH$_2$=CHCF$_2$$\underline{CF}_2$O, c); 126.3 ∅* (OCF$_2$$\underline{CF}_2$$\underline{CF}_2CF_2$O, c); 83.9 ∅* (O$\underline{CF}_2CF_2CF_2$$\underline{CF}_2$O, c).

(3) Addition of CF$_3$CH$_2$CH$_2$(CH$_3$)SiHCl to (X)

A mixture of (X) from above (0.102 mole), CF$_3$CH$_2$CH$_2$(CH$_3$)-SiHCl (0.31 mole) and a small quantity of H$_2$PtCl$_6$ catalyst was stirred and heated at 100-110°C for 8 hours in order to effect the addition of the silane to the olefin and, at the same time, to decompose any reverse-addition product that had formed. Distillation gave (XIII), b. p. 132-137°C/.03 mm, 62% yield. A center cut was taken for analyses: ^{19}F and ^{1}H nmr: (1) 126.6 ∅* (c); (2) 83.8 ∅*

$$\begin{array}{c}
CF_3 (10) \\
| \\
CH_2 (9) \\
| \\
CH_2 (8) \\
|
\end{array}$$

$$\{CF_2\text{-}CF_2\text{-}O\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}CH_2\text{-}\underset{\underset{CH_3(7)}{|}}{Si}\text{ - }Cl\}_2$$
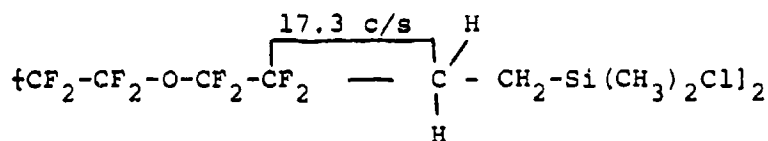(1) (2)   (3) (4) (5) (6)

(c); (3) 87.7 ∅* (c); (4) 120.1 ∅* (t, J = 17 cps); (5) and (9) 7.9 τ (c,and overlaying other absorptions); (6) and (8) 8.9 τ (c, and overlaying other absorptions); (7) 9.53 τ (s); (10) 69.4 ∅* (t, 6.9 c/s).

Anal. Calcd. for C$_{20}$H$_{22}$Cl$_2$F$_{22}$O$_2$Si$_2$: C, 28.61; H, 2.64; Cl, 8.45; F, 49.79. Found: C, 28.7; H, 2.6; Cl, 8.3; F, 49.6.

Three lower boiling fractions were obtained, b.p. 31-132°C/.03 mm, and these are assumed to contain the olefin from decomposition of the respective reverse-addition product(s).

b.　　**Preparation of $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XIV)**
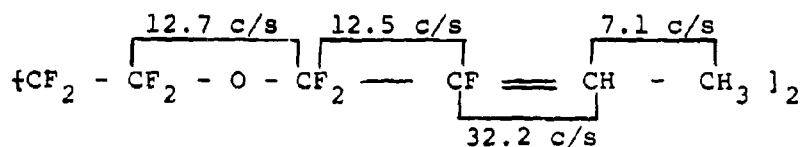
A mixture of (X) (0.57 mole), $(CH_3)_2SiHCl$ (0.17 mole) and a small quantity of H_2PtCl_6 catalyst was heated at reflux (bath temperature $\underline{ca}$. 60°C) for $\underline{ca}$. 12 hours. The unreacted $(CH_3)_2SiHCl$ was removed by distillation and the residual material heated at 150°C for 2-3 hours to decompose the reverse-addition product. A sample was obtained for analyses by redistillation, b.p. 88°C/.01 mm. Distillation gave (XIV), b.p. 79-86°C/.01 mm (45% yield): [19]F and ^{1}H nmr (coupling constants are given on the drawn structure);

$$\underbrace{[CF_2-CF_2-O-CF_2-CF_2}_{}\overset{\overbrace{17.3\ c/s}}{—}\ \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}\diagup - CH_2-Si(CH_3)_2Cl]_2$$

9.56 τ (CH_3, c); 8.96 τ ($Si\underline{CH}_2$, c); 7.89 τ ($\underline{CH}_2CF_2$, AB pattern); 120.1 φ* ($CH_2\underaccent{\sim}{CF}_2$, c); 87.8 φ* ($CH_2CF_2\underaccent{\sim}{CF}_2O$, c); 83.9 φ* ($O\underaccent{\sim}{CF}_2CF_2CF_2\underaccent{\sim}{CF}_2O$, c); 126.3 φ* ($OCF_2\underaccent{\sim}{CF}_2\underaccent{\sim}{CF}_2CF_2O$).

Anal. Calcd. for $C_{16}H_{20}Cl_2F_{16}O_2Si_2$: C, 28.45; H, 2.98; Cl, 10.50; F, 45.0. Found: C, 28.5; H, 2.9; Cl, 10.3; F, 45.2.

As noted above, a lower boiling product was obtained in the reaction of the organo-H-silanes with the straight-chain olefins. In the above reaction, spectroscopic examination of one fraction, cut 1, b.p. 30-56°C/.025 mm, indicated the presence of both $CH_3CH=CF\text{\textasciitilde}$ and $\text{\textasciitilde}CH_2CH_2Si(CH_3)_2Cl$ end-groups, probably from a mixture of all possible combinations of the two end-groups. Spectroscopic analyses of this material, estimated by nmr to contain approximately 90% of the diene illustrated below, showed: ir, 5.8 τ (CH=CF); nmr (coupling constants as shown):9.57 τ (CH_3,

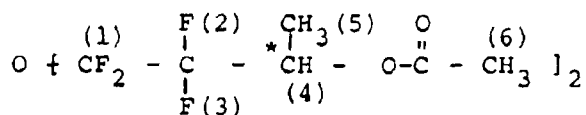$$\begin{array}{c} \overbrace{\text{12.7 c/s}} \quad \overbrace{\text{12.5 c/s}} \qquad \overbrace{\text{7.1 c/s}} \\ \text{\textbardbl CF}_2 - \text{CF}_2 - \text{O} - \text{CF}_2 \underline{\hspace{1cm}} \text{CF} = \text{CH} - \text{CH}_3 \text{]}_2 \\ \underbrace{\hspace{2cm}}_{\text{32.2 c/s}} \end{array}$$

double miltiplet); 4.42 τ (CH, double quartet); 84.∅* (O$\underset{\sim}{C}$F$_2$CF$_2$, b); 126.2 ∅* (OCF$_2$$\underset{\sim}{C}F_2$$\underset{\sim}{C}F_2CF_2$O, m); 75.3 ∅* (=CF$_2$$\underset{\sim}{C}F_2$, quartet).

c.   Preparation of O[CF$_2$CF$_2$CH$_2$CH$_2$Si(CH$_3$)(CH$_2$CH$_2$CF$_3$)Cl]$_2$ (XV)

(1)   O[CF$_2$CF$_2$CH(O$_2$CCH$_3$)CH$_3$]$_2$ (XI)

The diacetate (XI) was prepared by the procedure described above. In a typical reaction, O[CF$_2$CF$_2$CO$_2$CH$_3$]$_2$ (0.25 mole) was reacted with a mixture of methyl magnesium iodide and iso-propyl magnesium bromide prepared from CH$_3$I (0.60 mole), isopropyl bromide (0.75 mole), and magnesium turnings (1.35 g-atom). Re-action of the crude alcohol with acetyl chloride (0.65 mole) and distillation afforded (XI), b.p. 70-130°C/14 mm, 64% pure by VPC (44% yield by VPC analysis). A pure sample was obtained for analyses by redistillation, b.p. 111°C/12 mm. [19]F and ^{1}H nmr patterns are complex due to the presence of isomers caused by the asymmetric carbon atom*, and show the following absorptions:

$$\begin{array}{c} (1) \quad \overset{F}{\underset{F}{|}}(2) \quad \overset{*}{\underset{}{}}\overset{CH_3}{\underset{}{|}}(5) \quad \overset{O}{\underset{}{\parallel}} \quad (6) \\ O \text{\textbardbl} CF_2 - \underset{F(3)}{\overset{(2)}{C}} - \underset{(4)}{CH} - O-C - CH_3 \text{]}_2 \end{array}$$

(1) 85.3 ∅* (complex A$_2$B$_2$ due to d and l forms); (2) 122.3 ∅*, part of an AB type pattern, J$_{AB}$ = 275 c/s (doublet, J = 6.2 c/s); (3) 135 ∅*, part of an AB type pattern (d, J = 16 c/s); (4) 4.54 τ and 4.6 τ, double 5-fold due to the presence of two isomers; (5) 8.6 τ (d, J = 6.2 c/s); (6) 7.96 τ (s); some further structure is also evident due to d and l isomers.

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The intermediate alcohol from the Grignard reaction was never obtained in a pure state since it codistilled with other alcohols which were also obtained from the mixed Grignard reaction. It was always converted to the acetate ester without any further attempts at purification.

Since excellent yields of $O[CF_2CF_2C(CH_3)=CH_2]_2$ were obtained from the sulfuric acid dehydration of $O[CF_2CF_2C(CH_3)_2OH]_2$, attempts were made to dehydrate $O[CF_2CF_2CH(OH)CH_3]_2$ in a similar fashion.

Dehydration of $O[CF_2CF_2CH(OH)CH_3]_2$ with sulfuric acid in the manner described in 1b. above resulted in extensive decomposition as evidenced by the formation of black tars and evolution of SiF_4. In a second attempt, an effort was made to distill the olefin from the reaction mixture as it formed. This resulted in the formation of a white, intractable solid, probably as a result of the polymerization of the olefin.

Dehydration of $O[CF_2CF_2CH(OH)CH_3]_2$ with P_2O_5 met with similar success. Heating an intimate mixture of the alcohol (30.6 g) and P_2O_5 (40 g) resulted in formation of black tars and evolution of SiF_4. The small amount of distillate collected was processed by washing with water. This gave 2.0 g of material which contained approximately 50% olefin by VPC analysis.

(2) Preparation of $O[CF_2CF_2CH=CH_2]_2$ (XII)

Formation of (XII) from (XI) was effected by pyrolysis as described above. As noted, three preliminary experiments with $CF_3(CF_2)_6CH(O_2CCH_3)CH_3$ and finally with (XI) itself pointed toward the 500+ °C range. These preliminary pyrolyses with the latter acetate are summarized in the following table.
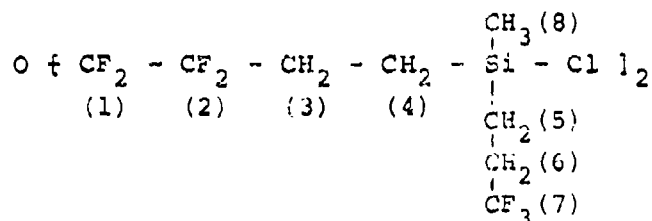
Pyrolysis of $O[CF_2CF_2CH(O_2CCH_3)CH_3]_2$

Reaction[a]		Product[b] (%)			
T, °C	N_2 (cc/min)	Wt. Pyrolyzate (g)	Diene	Half-Pyrolyzed	Unreacted
500	25	1.4	40	40	20
535	25	1.7	50	--	--
535	10	1.6	55	--	--
550	10	1.4	65	--	--
550	25	1.4	79	18	3

a) 2.0 g of diacetate added in 10-15 min.; b) product analysis by VPC area measurements on diene, half-pyrolyzed and unreacted ester.

In a typical reaction, pyrolysis of (XI) (126 g, .32 mole, 90% purity) at 570°C and 25 ml/min N_2 flow rate gave a 65% yield of processed, distilled (XII), b.p. 119°C/atm. press., ir (neat) 6.0 τ (C=C), ^{19}F and ^{1}H nmr, ø* 88.5 (OCF$_2$, s); 118.4 ø* (OCF$_2$CF$_2$, d with J = 8.4 c/s); 4.2 τ (CH=CH$_2$, c).

(3) Addition of $CF_3CH_2CH_2(CH_3)SiHCl$ to (XII)

A mixture of (XII), $CF_3CH_2CH_2(CH_3)SiHCl$ and H_2PtCl_6 was stirred at room temperature until an exothermic reaction occurred (approximately 30 minutes) and then heated at 110° for 24 hours to decompose any reverse-addition product which may have formed. Distillation of the reaction mixture gave 6.7 g (45% yield) of (XV), b.p. 117°C/.01 mm. The nmr spectra were in agreement with the assigned structure and had the following absorptions: (1) 87.9 ø*; (2) 119.9 ø* (c); (3) and (6) ca. 7.90 τ (c); (4) and (5) ca. 8.92 τ (c); (7) 69.2 ø*; (8) 9.54 τ (s).

$$O \{ CF_2 - CF_2 - CH_2 - CH_2 - \underset{\underset{\underset{CF_3\,(7)}{|}}{\underset{\underset{CH_2\,(6)}{|}}{\underset{CH_2\,(5)}{|}}}}{\overset{\overset{CH_3\,(8)}{|}}{Si}} - Cl \}_2$$

$$\phantom{O\{} (1) \quad (2) \quad (3) \quad (4)$$

Anal. Calcd. for $C_{16}H_{22}Cl_2F_{14}OSi_2$: C, 30.82; H, 3.56; Cl, 11.38; F, 42.67. Found: C, 31.1; H, 3.6; Cl, 11.1; F, 42.6.

d. Preparation of $O[CF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XVI)

A mixture of (XII) (0.106 mole), $(CH_3)_2SiHCl$ (0.53 mole) and a small quantity of H_2PtCl_6 was stirred at room temperature until an exothermic reaction occurred (50 min.) and then refluxed ca. 12 hours. This mixture was preheated to 90-100° for 2-3 hours to decompose any reverse-addition product and then (XVI) isolated by distillation, b.p. 69-72°C/.01 mm, (65% yield). Redistillation afforded an analytical sample: [19]F and ^{1}H nmr: (1) 88.1 ϕ^* (s);

$$O \{ CF_2 - CF_2 - CH_2 - CH_2 - Si(CH_3)_2 - Cl \}_2$$

$$\phantom{O\{} (1) \quad (2) \quad (3) \quad (4) \quad\quad (5)$$

(2) 120.0 ϕ^* (t, J = 16.8 c/s); (3) 8.9 τ (c, half of A_2B_2 pattern, but split into a triplet by No. 2, CF_2 group); (4) 8.9 τ (c, other part of A_2B_2); (5) 9.52 τ (s).

Anal. Calcd. for $C_{12}H_{20}Cl_2F_8OSi_2$: C, 31.8; H, 4.6; F, 33.2. Found: C, 31.7; H, 4.4; F, 33.1.

As in the preparation of $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ described above, a lower boiling product was obtained (ca. 30% of the total product by weight). Spectral data indicate that it too contains the $CH_3-CH=CF\sim$ moiety from elimination of $(CH_3)_2SiClF$ from the $CH_3CH[Si(CH_3)_2Cl]CF_2\sim$ moiety.

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e.   Attempted Preparation of $CF_3(CF_2)_6CH_2CH_2Si(CH_3)_2Cl$

(1) $CF_3(CF_2)_6CH(O_2CCH_3)CH_3$

The intermediate alcohol, $CF_3(CF_2)_6CH(OH)CH_3$ was prepared as described above, b.p. 35°C/1 mm (80% yield): ir neat), 3.0 μ (OH). ^{19}F and ^1H nmr: ∅* 81.6 (C$\underset{\sim}{F}_3$, t), 126.4 (CF$_3$C$\underset{\sim}{F}_2$, b), 121.9 [(C$\underset{\sim}{F}_2$)$_5$CH, b], τ 5.59 (C$\underset{\sim}{H}$, c), 8.61 (C$\underset{\sim}{H}_3$, d), 7.03 (O$\underset{\sim}{H}$, d).

Anal. Calcd. for $C_9H_5F_{15}O$: C, 26.10; H, 1.22; F, 68.82. Found: C, 26.5; H, 1.2; F, 69.1.

Reaction of the alcohol with acetyl chloride gave the acetate, b.p. 41°C/1 mm (90%): IR (neat) 5.6 μ (C=O). ^{19}F and ^1H nmr: 8.59 τ (CH$_3$, d); 4.50 τ (CH, m and coupled to CH$_3$ and 2 adjacent F atoms); 81.0 ∅* (CF$_3$); 126.4 ∅* (CF$_3$C$\underset{\sim}{F}_2$-); 122.1 ∅* [(C$\underset{\sim}{F}_2$)$_5$].

(2) $CF_3(CF_2)_6CH=CH_2$

Pyrolysis of $CF_3(CF_2)_6CH(O_2CCH_3)CH_3$ was effected by the procedure described above at 500°C. A 112 g sample of acetate was added to the pyrolysis chamber over an 8 hour period. The pyrolyzate (98.6 g) was washed with water and dried. Distillation gave 7 fractions, b.p. 52-165°C/atm. press. VPC analysis showed the presence of ca. 20 g of olefin with the remaining product divided among about 10 compounds. Since the olefin could not be purified by distillation, addition of silane was not attempted.

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3. **Bis-α,ω⁻{4⁻{Diorganochlorosil}⁻Propyloxy}⁻Perfluoroalkylene Oxide Precursors**
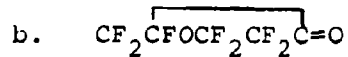
a. $\underline{CF_2=CFOCF_2CF_2CFO}$

Prepared by pyrolyzing $O(CF_2CF_2CO_2Na)$. A colorless liquid; ν 5.29 μ (C=O), 5.42 μ (C=C); n.m.r. spectrum: (1) -23.4 Ø*

$$(4)F\diagdown\diagup F(5)$$
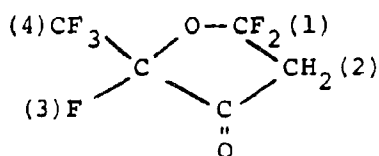$$C=C$$
$$(6)F\diagup\diagdown O-CF_2-CF_2-\overset{\overset{\displaystyle O}{\|}}{CF}$$
$$(2)(3)(1)$$

triplet (J = 8.0 c/s); triplet (J = 5.9 c.s); (2) 87.8 Ø* (c);
(3) 121.3 Ø*, double (J = 8.0 c/s) triplet (J = 3.7 c/s);
(4) 114.3 Ø*, double (J = 8.4 c/s) doublet (J = 64.5 c/s);
(5) 136.5 Ø*, double (J = 64.5 c/s) triplet (J = 5.6 c/s);
(6) 122.3 Ø*, double (J = 109 c/s) double (J = 83.6 c/s) triplet (J = 5.7 c/s).

Anal. Calcd. for $C_5F_8O_2$: C, 24.6; F, 62.0. Found C, 24.0; F, 61.2.

b. $\underline{\overset{\frown}{CF_2CFOCF_2CF_2}C=O}$

The infrared showed absorption at 5.44 μ (C≐O); ^{19}F nmr spectrum: (1) 79.7 and 93.4 Ø*, an AB type pattern with

$$(4)CF_3\diagdownO-CF_2(1)$$
$$C$$
$$\diagup\diagdown CH_2(2)$$
$$(3)FC$$
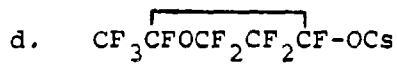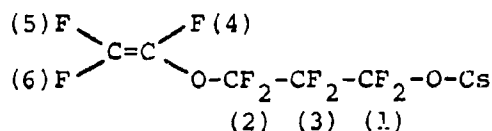$$\overset{\|}{\underset{O}{}}$$

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$J_{AB} = 134$ c/s [79.7 peak is a doublet (J = 9.0 c/s) and 93.4 peak is a triplet (J = 4.8 c/s)]; (2) 124.1 and 132.1 ø*, an AB type pattern, $J_{AB} = 294.8$ c/s [124.1 peak is a double (J = 7.9 c/s) five fold (J = 1.9 c/s), 132.1 peak is a doublet (J = 4.8 c/s)]; (3) 121.7 ø* (c); (4) 81.9 ø* double (J = 5.5 c/s) doublet (J = 1.9 c/s).

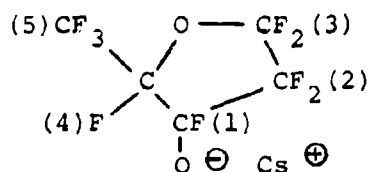Anal. Calcd. for $C_5F_8O_2$ (244): C, 24.6; F, 62.4. Found C, 23.7; F, 60.6.

Mol. Wt. 244.

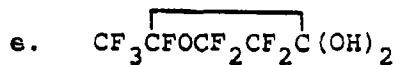c. $\underline{CF_2=CFOCF_2CF_2CF_2OCs}$

The nme spectrum shows: (1) 27.6 ø* (vb); (2) 85.5 ø*; (3) 123.7 ø*; (4) 133.3 ø*, double (J = 103 c/s) doublet (J = 60 c/s); (5) 116 ø*, double (J = 83 c/s) doublet (60 c/s); (6) 123.3 ø*, double (J = 103 c/s) doublet (83 c/s).
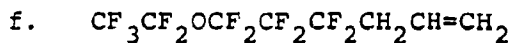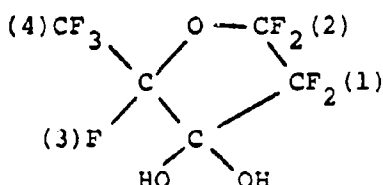

d. $\underline{CF_3CFOCF_2CF_2CF-OCs}$

The nmr spectrum shows: (1) 93.0 ø* (vb); (2) 124.2 and 137.6 ø*, AB type pattern with $J_{AB} = 248$ c/s; (3) 82.0 and 85.8 ø*, AB type pattern, $J_{AB} = 128$ c/s; (4) 123.1 ø*; (5) 79.4 ø*.

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e. $CF_3\overline{CFOCF_2CF_2C}(OH)_2$

Derived from addition of water to the ketone. ^{19}F nmr spectrum shows: (1) 124.9 and 136.1 ϕ^*, AB pattern with J = 238 c/s; (2) 81.4 and 85.5 ϕ^*, AB pattern with J = 132 c/s; (b) 124.2 ϕ^*; (4) 79.9 ϕ^*.

f. $CF_3CF_2OCF_2CF_2CF_2CH_2CH=CH_2$

^{19}F nmr spectrum shows: 86.4 ϕ^* ($CH_2O\underline{CF}_2$); 129.4 ϕ^* ($CF_2\underline{CF}_2CF_2$); 84.3 ϕ^* ($CF_3CF_2O\underline{CF}_2$); 89.0 ϕ^* ($CF_3\underline{CF}_2$); 87.6 ϕ^* (CF_3).

B. MISCELLANEOUS SILICON COMPOUNDS

1. Organo-H-Chlorosilanes

a. Preparation of $CF_3CH_2CH_2(CH_3)SiHCl$

(1) Preparation of $CF_3CH_2CH_2(CH_3)SiCl_2$

A total of 4.53 lbs of $CF_3CH_2CH_2(CH_3)SiCl_2$ was prepared for conversion to the monochloro-H-silane. In a typical reaction, 394 g (4.1 mole) of $CF_3CH=CH_2$, 954 g (8.2 mole) of CH_3SiHCl_2, and H_2PtCl_6 catalyst were added to a Hastelloy pressure vessel and heated at 175°C with shaking for 3 days. Distillation of the reaction mixture gave 727 g (81% yield based

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on 95% purity) of $CF_3CH_2CH_2(CH_3)SiCl_2$, b.p. 122°, of sufficient
purity for use in the next step. The nmr spectrum was in agreement

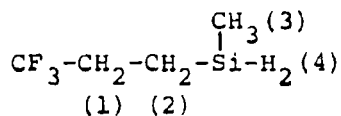$$CF_3-CH_2-CH_2-\underset{\underset{(1)\ (2)}{}}{\overset{\overset{CH_3\ (3)}{|}}{Si}}-Cl_2$$

with the assigned structure and showed the following absorptions:
(1) ca. 7.72 τ (c); (2) 8.70 τ (c); (3) 9.17 τ (s).

(2) Preparation of $CF_3CH_2CH_2SiH_2$

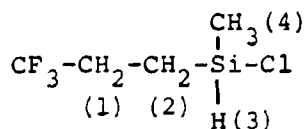The procedure of Anderson[9] was adopted. In a typical
reaction, 422 g (2 mole) of $CF_3CH_2CH_2(CH_3)SiCl_2$ was added drop-
wise to 76 g (2 mole) of $LiAlH_4$ in 1000 ml of di-n-butyl ether
cooled in an ice bath (0-5°). After the addition was completed
the reaction mixture was refluxed until the head temperature had
dropped to ca. 60°C. Distillation of the unhydrolyzed reaction
mixture gave 275 g (90% yield based on 93% purity) of $CF_3CH_2CH_2$-
$(CH_3)SiH_2$, b.p. 61°, of sufficient purity for use in the next
step. The ^{1}H nmr spectrum showed the following absorptions: (1)
7.88 τ (c); (2) 9.05 τ (c); (3) 9.82 τ (t); (4) 6.20 τ (six-fold);
molecular weight 143, theory requires 142.

$$CF_3-CH_2-CH_2-\underset{\underset{(1)\ (2)}{}}{\overset{\overset{CH_3\ (3)}{|}}{Si}}-H_2\ (4)$$

(3) Reaction of $CF_3CH_2CH_2(CH_3)SiH_2$ with Metal
Chlorides

The procedure of Anderson[9] was modified and used for
this preparation. Trifluoropropylmethylsilane (240.5 g, 1.7 mole)

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from the previous reaction was placed in a three-necked flask
fitted with a water condenser connected to a -78° gas trap fitted
with a Drierite drying tube and the flask cooled in an ice-bath
(0-5°). Mercuric chloride (461 g, 1.7 moles) was added to the
silane in four equal portions as rapidly as the exotherm from
the preceding addition would allow. After all the mercuric
chloride had been added the liquid in the -78° trap (primarily
starting material) was added back to the reaction and the reaction
mixture refluxed until the reflux temperature reached the boiling
point of the product. The product was then distilled out at
atmospheric pressure and finally under vacuum (8-12 mm). Redis-
tillation gave 233 g (75% yield based on 96% purity) of CF_3CH_2-
$CH_2(CH_3)SiHCl$, b.p. 99°, of sufficient purity for the subsequent
olefin addition reactions. The H^1 nmr spectrum of the product
was in agreement with the assigned structure and showed the
following absorptions: (1) 7.8 τ (c); (2) 8.9 τ (c); (3) 5.13 τ;
(4) 9.47 τ.

$$CF_3-\underset{(1)}{CH_2}-\underset{(2)}{CH_2}-\underset{H\,(3)}{\overset{CH_3\,(4)}{\underset{|}{\overset{|}{Si}}}}-Cl$$

b. Preparation of $(CF_3)_2CFO(CH_2)_3(CH_3)SiCl_2$ and

$\overline{CF_2CF_2CH_2CH}(CH_3)SiCl_2$

Heptafluoroisopropoxypropylmethyldichlorosilane was pre-
pared by the method of Pittman[10] and is described in the discussion.
As noted there, one reaction of $(CF_3)_2CFOK$ with CH_2=$CHCH_2Br$ at
80-90°C as recommended[10] gave very little of the desired allyl ether.
A heavy odor of allyl bromide was detected during the reaction and
is suspected to be due to entrainment of CH_2=$CHCH_2Br$ by $(CF_3)_2C$=O
produced from thermal decomposition of the perfluoroalkoxide.

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Tetrafluorocyclobutylmethyldichlorosilane was prepared by the method of Park, Grover, and Lacher[11] and purified by distillation.

2. Acetoxysilanes

The acetoxysilanes were prepared in nearly quantitative yield by reaction of a slight excess of acetic anhydride with the appropriate chlorosilane at 50-90°C for about 24 hours. The triacetoxysilanes prepared were methyltriacetoxysilane, b.p. 98-99°C/10 mm (solidified on standing); 3-(heptafluoroisopropoxy)-propyltriacetoxysilane, b.p. 116°C/.07 mm, and methylvinyldiacetoxysilane, b.p. 70-71°C/9 mm.
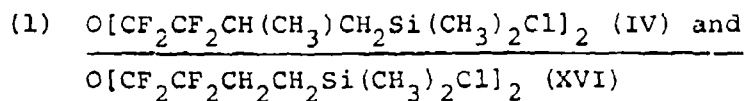
C. FLUOROCARBON ETHER-BRIDGED SILOXANE POLYMERS

1. Hydrolysis of Chlorosilanes

a. Water Hydrolysis

A sample of $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$ (0.02 mole) was added with stirring to water (0.32 mole) at room temperature. The heavy oil which separated out of the water was washed three times with water, taken up in ether and the ether solution washed with water until neutral and then dried $(CaSO_4)$. Evaporation of the ether gave a clear, colorless oil with a $\overline{M}n$ of 7100 and silanol functionality (f) equal to or less than 0.7 by measurement of active hydrogen.

b. Water Hydrolysis and Polymerization

(1) $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$ (IV) and

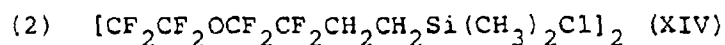$O[CF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XVI)

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An ether solution of (XVI) was shaken with water for one hour. The ether layer was then removed and dried over $CaSO_4$. After removal of the ether, a viscous liquid remained. The infrared spectrum of this liquid indicated the presence of SiOH groups in the molecule (broad absorption at ca. 3.0 μ).

The residue was then heated at 150°C for 15 minutes in the presence of a trace quantity of H_2SO_4. After cooling, the material was dissolved in ether, washed with H_2O to remove H_2SO_4, and then dried over $CaSO_4$. After filtration an excess of ClSi-$(CH_3)_3$ was added to end-cap the polymer and the mixture was heated at 100°C in vacuo to remove both ether and excess $ClSi(CH_3)_3$. $\overline{M}n$ (VPO) was 6300 in Freon-113.

Another sample of the polymer was prepared by treating (XVI) with water in ether without the addition of H_2SO_4. After stirring for one hour the residue was then heated at 150°C in vacuo for one hour. The infrared spectrum of the residue showed no evidence of SiOH bonds, and had an $\overline{M}n$ = 5300 and a Tg of -76°. This sample showed weight losses by TGA in air of 1%, 1.5%, and 50% by 300°C, 350°C, and 400°C, respectively.

The procedure described above was used for polymerizing $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$. This product had a $\overline{M}n$ of 6900 and a Tg of -60°. TGA in air showed weight losses of 3%, 10%, and 40% by 300°C, 350°C, and 400°C, respectively.

(2) $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XIV)

The silyl chloride (.0074 mole) was added dropwise to ether (50 ml) saturated with water (.03 mole). The ether solution was washed with water and dried ($CaSO_4$). Removal of the ether by evaporation gave a residual liquid with a $\overline{M}n$ = 1300 and which showed no -OH absorption in the infrared.
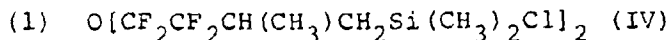
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Polymerization was accomplished by reacting the liquid with one drop of 36N H_2SO_4 for 8 hours at room temperature and then for 32 hours at 110°C/0.4 mm. Processing as described above gave a polymer (which still showed no -OH absorption in the infrared) with a $\overline{M}n$ = 3000 and a Tg of -76°. TGA analysis in air showed weight losses of 4.5%, 8%, and 12.5% by 300°C, 350°C, and 400°C, respectively.

c. Base Hydrolysis and Polymerization

A sample of (IV) was hydrolyzed with saturated aqueous sodium bicarbonate solution and the product taken up in ether and washed neutral with water and dried ($CaSO_4$). Removal of the ether gave a clear, colorless hydrolyzate with a $\overline{M}n$ = 590.

The hydrolyzate was polymerized by heating at 100°C in vacuo for 2 days in the presence of a catalytic amount of sulfuric acid. After removal of the sulfuric acid, a viscous polymer was obtained with a $\overline{M}n$ = 12,200.

d. Hydrolysis with Aqueous Sodium Bicarbonate

(1) $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$ (IV)

A sample of (IV) (0.14 mole) was hydrolyzed by adding it dropwise over a 2 hour period to a rapidly stirred saturated aqueous sodium bicarbonate solution (0.34 mole in 225 ml of H_2O). The resulting hydrolysis reaction mixture was then refluxed for 2 hours. The organic product was taken up in ether and the ether solution washed with a saturated aqueous sodium chloride solution until the washes were neutral to pH paper and then dried over $CaSO_4$. Evaporation of the ether gave a fluorocarbon ether-bridged siloxane hydrolyzate with a $\overline{M}n$ = 1950, f = 1.6, and a bulk viscosity at 23°C of 2360 cps.

A 167 g sample of (IV) was hydrolyzed with sodium bi-
carbonate solution as described above and the reaction mixture
allowed to stand overnight. The mixture was then heated at reflux
for 2 hours, the aqueous layer was decanted, and the residual sil-
anol was washed several times with water and then dried by azeo-
tropic distillation with cyclohexane. The resulting polymer had
a $\overline{Mn}$ = 2500 and f = 1.6. Devolatilization of a portion of this
material at 190-200°C $\underline{in}$ $\underline{vacuo}$ overnight gave a residual oil with
a $\overline{Mn}$ = 3500 and f = 1.6.

(2) $O[CF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XVI)

An ether solution of (XVI) (0.07 mole in 150 ml of ether)
was added to a stirred saturated aqueous sodium bicarbonate solu-
tion (0.25 mole in 200 ml of water). The ether layer was separated
from the aqueous layer and the ether layer washed three times with
a saturated aqueous sodium chloride solution and then dried over
$CaSO_4$. Evaporation of the ether gave a clear, colorless oil with
a $\overline{Mn}$ of 740. Heating the hydrolyzate at 125-150°C/.01 mm for 5
hours gave a clear, viscous polymer with a $\overline{Mn}$ of 9500, and bulk
viscosity of 35,000 cps at 23°C.

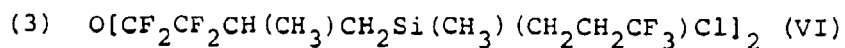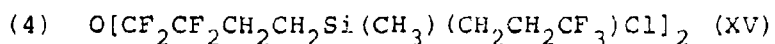(3) $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)(CH_2CH_2CF_3)Cl]_2$ (VI)

A sample of (VI) (0.14 mole) was hydrolyzed by adding it
dropwise over a one hour period to a vigorously stirred saturated
aqueous sodium bicarbonate solution (0.31 mole in 175 ml of water).
The resulting hydrolysis reaction mixture was then stirred and
heated at 100-110°C for 10 hours. The organic product was taken up
in ether and the ether solution washed with dilute hydrochloric
acid and then with water (until the water washes were neutral) and
then dried over $CaSO_4$. Evaporation of the ether gave a fluorocarbon
ether-bridged siloxane hydrolyzate product which was a clear,

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colorless oil with a $\bar{M}n$ = 800, f = 2, and a bulk viscosity of 3850 cps at 22°C. Distillation of a portion of the latter product gave monomer silanol, b.p. 150°C/.01 mm with a $\bar{M}n$ = 600 and a residue with a $\bar{M}n$ = 1060.

(4) $O[CF_2CF_2CH_2CH_2Si(CH_3)(CH_2CH_2CF_3)Cl]_2$ (XV)

A sample of (XV) (0.13 mole) was hydrolyzed by the procedure described immediately above and the reaction mixture then heated at 100-110°C for 8 hours. The recovered fluorocarbon ether-bridged siloxane hydrolyzate product was a clear, colorless oil with a $\bar{M}n$ = 1200 and a f = 1.7.

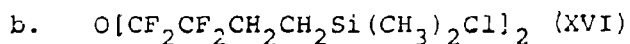## 2.   Polymerization with Aqueous Sodium Bicarbonate

a. $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)_2Cl]_2$ (IV)

A sample of (IV) (0.24 mole) was added to a slight excess of vigorously stirred saturated aqueous sodium bicarbonate solution over a 1.75 hour period. The reaction mixture was then stirred and heated 2 hours at 100°C. Then in succession was added 1.9 g (0.023 mole) of sodium bicarbonate in 90 ml of water and a second sample of hydrolyzate with a $\bar{M}n$ = 1950. This mixture was stirred and heated at 100°C for 42 hours. The organic product was taken up in ether and washed with saturated aqueous sodium chloride until neutral and dried over $CaSO_4$. Evaporation of the ether was followed by devolatilization at 250°C/.05 mm for one hour. The product had a $\bar{M}n$ = 3200, f = 1.4, and bulk viscosity of 2500 cps at 25°C.

b. $O[CF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XVI)

A 14 g (0.03 mole) sample of (XVI) was hydrolyzed as described in (a) above and the reaction mixture was heated at 100°C for 7 hours. The product was recovered as described in (a) above

and then devolatilized at 210-253°C/.15 mm over a 5 hour period. This gave a clear oil with a $\overline{M}n$ = 6600 and silanol functionality <.66.

c. $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)_2Cl]_2$ (XIV)

A sample of (XIV) (0.02 mole) was hydrolyzed with sodium bicarbonate as described in (2a) above and the reaction mixture was heated at ca. 100°C for 8 hours. The hydrolyzate product was recovered as described in (2a) above and was a clear, colorless oi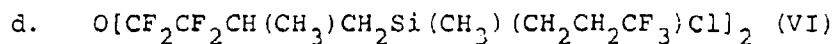l with $\overline{M}n$ = 5000. Devolatilization of the latter product by heating at 200-210°C/.1 mm for 8 hours and then at 260°C/.01 mm for 4.5 hours gave a siloxane product with a $\overline{M}n$ of 9100 and functionality of 1.1.

d. $O[CF_2CF_2CH(CH_3)CH_2Si(CH_3)(CH_2CH_2CF_3)Cl]_2$ (VI)

A sample of (VI) (0.14 mole) was hydrolyzed with sodium bicarbonate by the procedure of (2a) above and the reaction mixture was heated at ca. 100°C for 53 hours. Recovery of the product by the method described in (2a) above was followed by devolatilization at 230-240°C/.01 mm for 18 hours to give a clear, colorless oil with a $\overline{M}n$ = 2500, a f = 2.5, and a bulk viscosity of 31,200 at 23-25°C.

e. $O[CF_2CF_2CH_2CH_2Si(CH_3)(CH_2CH_2CF_3)Cl]_2$ (XV)

A sample of (XV) (0.12 mole) was hydrolyzed with a saturated aqueous sodium bicarbonate solution (0.29 mole in 190 ml of water) by the procedure of (2a) above and the hydrolysis reaction mixture then heated at ca. 100°C for 48 hours. Recovery of the product as described in (2a) above was followed by devolatilization

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at 235°C/.01 mm for 15 hours to yield a clear oil with a $\bar{M}n$ = 4700, a f = 2.2, and a bulk viscosity of 27,400 cps at 23°C.

f. $[CF_2CF_2OCF_2CF_2CH_2CH_2Si(CH_3)(CH_2CH_2CF_3)Cl]_2$ (XIII)

A sample of (XIII) (0.061 mole) was hydrolyzed as described in (2a) above and the hydrolysis reaction mixture was heated at ca. 100°C for 12 hours. Recovery of the product by the procedure described in (2a) above was followed by devolatilization by heating at 195-250°C/.25 mm over a 9 hour period to give a clear, viscous oil with a $\bar{M}n$ = 12,500, a f = 1.6, and a bulk viscosity of 22,800 at 25°C.

3. Polymerization with Dilute Sodium Carbonate

a. Type I Hydrolyzate

A mixture of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH(CH_3)CF_2CF_2OCF_2CF_2-CH(CH_3)CH_2Si(CH_3)(CH_2CH_2CF_3)O\}_x H$ (7.5 g, $\bar{M}n$ = 670, f = 1.8) and aqueous sodium carbonate (2 g in 35 ml of water) was stirred and heated under reflux for 26 hours. The product was taken up in ether, the ether solution washed with water until the water washes were neutral and then dried over $CaSO_4$. Evaporation of the ether gave a siloxane product with a $\bar{M}n$ of 900 and silanol functionality of 1.8. Reaction of the latter product with a second aqueous sodium carbonate solution (2 g in 35 ml of water) at reflux for 78 hours (104 hrs. total) and recovery of the product as described above gave a siloxane polymer with a $\bar{M}n$ = 1450 and a f = 2.2.

b. Type II Hydrolyzate

A mixture of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2CF_2Cl\}_2OCF_2CF_2CH_2-CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_x H$ (21 g, $\bar{M}n$ = 1150) and aqueous sodium carbonate (2 g in 100 ml of water) was stirred and heated at reflux

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for 37 hours. The organic product was taken up in ether and the ether solution was washed with a saturated aqueous sodium chloride solution and dried over $CaSO_4$. Evaporation of the ether gave a fluorocarbon ether-bridged siloxane product with a $\overline{M}n$ of 2150 and a silanol functionality of 1.6.

A second type II hydrolyzate sample (62 g, $\overline{M}n \simeq 1150$) and aqueous sodium carbonate (14 g in 200 ml of water) were heated at reflux for 23 hours and processed as described above. This gave a clear, colorless siloxane product with a $\overline{M}n = 7500$, a $f \simeq 0.75$, and a bulk viscosity at 25°C of 46,400 cps.

4. Polymerization with Non-Bond Rearranging Catalysts

a. Type I Hydrolyzate and Dibutyl Tin Diacetate

A mixture of $HO\{(CH_3)_2SiCH_2(CH_3)CHCF_2CF_2OCF_2CF_2CH(CH_3)-CH_2Si(CH_3)_2O\}_xH$ from C1d above (ca. 150 g, $\overline{M}n = 2500$, $f = 1.6$), 2 drops of dibutyl tin diacetate and ca. 150 ml of cyclohexane was heated at reflux under a Dean-Stark trap for 2 days. The cyclohexane was then removed by evaporation on a rotating evaporator. About 37 g of the polymer was removed and heated one hour at 230°C. This gave an extremely viscous, ether soluble polymer with a $\overline{M}n = 16,000$. The remaining material was heated at 190°C in vacuo overnight. This gave a polymer of honey-like consistency with a $\overline{M}n \simeq 9800$ and a $f = 2$.

b. Type I Hydrolyzate with n-Hexylamine 2-Ethylhexoate

(1) In Benzene Solution

A mixture of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH(CH_3)CF_2CF_2OCF_2\overline{}CF_2CH(CH_3)CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$ (30 g, $\overline{M}n = 2550$, $f = 2.6$) and benzene (26 g) were brought to reflux under a Dean-Stark trap

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filled with benzene. Two drops (ca. .075 g) of n-hexylamine 2—ethylhexoate were added and refluxing continued for 16 hours. The benzene was then removed on a rotating evaporator under aspirator pressure ($\sim$13 mm) while heating the flask with a pan of hot water (ca. 50-60°C) and finally by heating at 90-120°C at 0.7 mm. The resulting polymer had a $\overline{M}n = 3250$.

The silanol from above was redissolved in 30 ml of benzene and brought to reflux as before. Three drops of catalyst were added (now a total of .00075 mole of catalyst present) and the mixture heated at reflux for 52 hours. The benzene was removed by heating under aspirator pressure and the polymer formed was dissolved in 100 ml of ether. The ether solution was washed with 6 portions of aqueous $NaHCO_3$ (0.012 mole per wash), and then 5 times with saturated aqueous sodium chloride and dried over $CaSO_4$. Removal of the ether gave a polymer (20.6 g) with a $\overline{M}n = 4700$ and a $f = 3.3$.

(2)   Neat Versus Solution Polymerization

Stirring a mixture of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH(CH_3)-CF_2CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$ (7.5 g, $\overline{M}n = 670$, $f = 1.8$) and a catalytic amount of n-hexylamine 2-ethylhexoate at room temperature gave a siloxane product with a $\overline{M}n = 900$. The latter (catalyst still present) was then heated and stirred at 120°C/.4 mm. The resulting siloxane polymer was taken up in ether and the ether solution was washed several times with a 10% aqueous sodium carbonate solution and then water and dried over $CaSO_4$. Evaporation of the ether gave a siloxane polymer with a $\overline{M}n = 2900$ and a silanol functionality of 1.5.

A second sample of the silanol used immediately above (7.5 g, $\overline{M}n = 670$, $f = 1.8$), benzene (25 ml) and a trace of n-hexylamine 2-ethylhexoate were stirred at 25°C for 25 hours and then

heated at reflux for 24 hours under a Dean-Stark trap. The benzene
was then removed by evaporation and the residue was taken up in
ether, washed several times with a 10% aqueous sodium carbonate
solution and then water and dried over $CaSO_4$. Evaporation of the
ether gave a polymer with a $\overline{M}n$ = 2800 and a f $\leqslant$0.3.

c. Type II Hydrolyzate and n-Hexylamine 2-Ethylhexoate

A mixture of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2CF_2CF_2OCF_2CF_2$-
$CH_2CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_x H$ ($\overline{M}n$ = 2150, f = 1.6) and a catalytic
amount of n-hexylamine 2-ethylhexoate were stirred at 25°C/0.4 mm
for 24 hours and then heated with stirring at 100°C/.4 mm for 10
minutes. This procedure gave a clear and colorless, rubbery siloxane
polymer.

d. Type I Hydrolyzate and Tetramethylguanidine Di-2-
Ethylhexoate

A solution of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH(CH_3)CF_2CF_2OCF_2$-
$CF_2CH(CH_3)CH_2Si(CH_3)(CH_2CH_2CF_3)O\}_x H$ ($\overline{M}n$ = 710, f = 1.8) in benzene
(25 ml) and a catalytic amount of tetramethylguanidine di-2-
ethylhexoate catalyst was heated at reflux for 23 hours and the
water of condensation was removed continuously with a Dean-Stark
trap. The benzene was removed by evaporation and the residual
siloxane polymer was taken up in ether. The ether solution was
then washed three times with dilute sodium hydroxide, then with
dilute hydrochloric acid and finally with water and dried over $CaSO_4$.
Evaporation of the ether gave a siloxane polymer with a $\overline{M}n$ = 4500,
a f $\leqslant$.3, and a bulk viscosity of 1,381,000 cps (23°C).

Attempted distillation of a sample of the polymer (9 g)
by heating at 200-260°C/.01 mm gave about 1 g of distillate, b.p.
81-92°C/.01 mm, which showed no -OH absorption in the infrared,

and had a molecular weight of 595 as opposed to a theoretical
value of 596 for the monocyclosiloxane. The nmr spectra were
complex, but in agreement with the structure of the monocyclo-
siloxane shown below: (1) centered at 84.5 ∅* (AB); (2) ca. 123 ∅*
(c and vb); (3) and (8) overlaying complex multiplets centered

$$
\begin{array}{c}
\quad\quad\quad\quad\quad\quad\quad\quad (1)\quad\ (2) \\
CF_2 - CF_2 - O - CF_2 - CF_2 \\
CH_3-C-H \quad\quad\quad\quad\quad\quad (3)H-C-CH_3(4) \\
CH_2 - Si - O - Si - CH_2 (5) \\
CF_3CH_2CH_2 \quad CH_3 \quad\ CH_3 \quad CH_2CH_2CF_3 \\
(6)\quad\ (7)\ (8)\ (9)
\end{array}
$$

at ca. 8 τ; (4) 8.8 τ (d); (5) and (7) complex overlaying AB types
centered at ca. 9.2 τ; (6) 9.77 τ (s) and 9.83 τ (s) due to two
different isomers; (9) 69.5 ∅* (t).

A 21 g sample of HO$\{(CH_3)_2SiCH_2(CH_3)CHCF_2CF_2OCF_2CF_2CH-$
$(CH_3)CH_2Si(CH_3)_2O\}_xH$ ($\overline{M}n = 1950$, f = 1.6) in 25 ml of benzene was
polymerized by heating at reflux for 10.5 hours in the presence of
a catalytic amount of tetramethylguanidine di-2-ethylhexoate.
Processing of the reaction product by the procedure described above
gave a siloxane product with a $\overline{M}n = 5900$ and a f ≮.6.

e. Type II Hydrolyzate and n-Hexylamine Di-2-Ethylhexoate

A 30 g sample of HO$\{(CH_3)(CF_3CH_2CH_2)SiCH_2CH_2CF_2CF_2OCF_2-$
$CF_2CH_2CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$ ($\overline{M}n = 1200$, f = 1.7) in 20 ml of
benzene was polymerized by heating at reflux for 16.5 hours in the
presence of a catalytic amount of n-hexylamine di-2-ethyl-
hexoate. Processing the product by the procedure described above
gave a polymer with a $\overline{M}n = 4560$ and a f ≮.46.

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f.   Type I Hydrolyzate and Tetramethylguanidine

A sample of $HO\{(CH_3)(CF_3CH_2CH_2)SiCH_2(CH_3)CHCF_2CF_2OCF_2CF_2-CH(CH_3)CH_2Si(CH_2CH_2CF_3)(CH_3)O\}_xH$ ($\overline{M}n$ = 670, f = 1.6) in 25 ml of benzene and containing a catalytic amount of tetramethyl-guanidine was polymerized by heating at reflux for 18 hours. This gave a polymer with $\overline{M}n$ = 6500 and a f $\leqslant$.65.

5.   Copolymerization Reactions

To a stirred ethereal solution of $HO\{(CH_3)_2SiCH_2(CH_3)CHCF_2-CF_2OCF_2CF_2CH(CH_3)CH_2Si(CH_3)_2O\}_xH$ ($\overline{M}n$ = 9800, f = 2) was added a solution containing the stoichiometeric quantity of vinylmethyl-dichlorosilane in ether. An equivalent quantity of triethylamine was then added and the precipitate removed by filtration. After removal of the ether there remained a viscous material which was shown by infrared spectroscopic analysis to contain vinyl groups. When samples of this product were heated with a dihydrosilane such as diphenyl silane in the presence of a catalyst such as platinum on charcoal, chloroplatinic acid or $H[PtCl_3 \cdot CH_2=CH_2]$, there was obtained a rubbery solid.

In a second copolymerization reaction, 32.5 g (0.067 mole) of (IV) and 0.5 g (0.0035 mole) of $CH_3(CH_2=CH)SiCl_2$ were added to a vigorously stirred saturated aqueous sodium bicarbonate solution (0.17 mole in 110 ml of water) and the resulting mixture heated at reflux for 24 hours. The organic product was dissolved in ether and washed until neutral with saturated sodium chloride solution and dried over $CaSO_4$. Evaporation of the ether and then devol-atilization of the residue by heating at 230°C/.1 mm for 11 hours gave 6 g of a slightly cloudy distillate which cleared on standing. The residue was a clear, colorless oil, $\overline{M}n$ = 3300, which clouded on standing.

D.   FLUOROCARBON ETHER-BRIDGED SILOXANE RUBBER COMPOUNDS

1.   Curing Procedures

a.   Unfilled Polymer

Initial curing reactions were carried out with a sample of polydimethylsiloxane ($\overline{M}n$ = 60,000, f = 2) and three triacetoxysilane curing agents.   The purpose of this effort was to establish satisfactory curing procedures for use with the silanol-ended fluorocarbon ether-bridged siloxanes.   With the unfilled polydimethylsiloxane, satisfactory results were obtained by mixing in a two to three fold excess of triacetoxysilane under ambient conditions, adding a curing catalyst and allowing the mixture to stand at room temperature.   With lead octoate catalyst, cures were obtained in 1 to 2 days and with tetraisopropyltitanate within a day.   This procedure was adopted for use with the unfilled fluorocarbon ether-bridged siloxane polymers.

b.   Filled Polymer

With filled polydimethylsiloxane ($\overline{M}n$ = 60,000, f = 2, 100 parts), cured rubbers were obtained within 24 hours without the above mentioned curing catalysts by mixing in 7-12 parts of vinyltriacetoxysilane.   Attempts to cure the filled samples with four or less parts of vinyltriacetoxysilane gave incomplete cures.   This procedure was adopted for use with the filled fluorocarbon ether-bridged siloxane polymers.

E.   FUNCTIONALLY-TERMINATED POLY(PERFLUOROALKYLENE OXIDES)

1.   Preparation of $CF_3CF_2OCF_2CF_2CFO$[20]

A 752 g aliquot of crude acid was neutralized with aqueous sodium hydroxide, then mixed with a second 752 g aliquot of acid

and the resulting mixture made strongly basic with calcium
hydroxide. Solids were removed from the basic mixture by filtra-
tion, the water removed from the filtrate by evaporation and the
solid salt exhaustively dried (72 hours) at 75-100°C/.1 mm to re-
move inert fluorocarbons. The salts were dissolved in 36N sulfuric
acid and a sample of purified acid isolated by distillation; b.p.
76-78°/52 mm, n_d^{25} 1.2885. Reported[20] b.p. 136°, n_d^{25} 1.283.

Chlorination of perfluoroethoxypropionic acid with phthaloyl
chloride gave perfluoroethoxypropionyl chloride,[20] b.p. 60-62°C,
98.5% pure by VPC. Reported b.p. 64°C/740 mm.

Reaction of neat perfluoroethoxypropionyl chloride with anhy-
drous potassium fluoride gave perfluoroethoxypropionyl fluoride,
b.p. 35-36°. Redistillation on a 12 in. Podbielniak column gave
three fractions: fraction 1, b.p. 35-35.5° (97% purity); fraction
2, b.p. 35.5-36° (98% purity); and fraction 3, b.p. 36° (99% purity).
Fraction 3 was used in the photolysis described below.

2.   Photolysis of $CF_3CF_2OCF_2CF_2CFO$

Perfluoroethoxypropionyl fluoride was allowed to vaporize into
a 500 ml quartz bulb and the gas (250 mm) irradiated with a 450
watt medium pressure ultraviolet lamp. Vapor phase chromatography
on a column of FS-1265 on chromosorb P, 12' x 1/4", showed carbonyl
fluoride, oxalyl fluoride, unreacted starting material and three
higher boiling products which were later identified   (YXII),
(XXIV), and (XXV). Several similar reactions afforded a sufficient
volume of liquid from which the three new compounds were obtained
in pure form by vapor phase chromatography on a column of FS-1265
on chromosorb P.

Liquid phase photolysis of perfluoroethoxypropionyl fluoride
(neat) afforded the same products as noted above, but gave signifi-
cantly smaller amounts of the two branched products.

a. $CF_3CF_2OCF_2CF_2CF_2CF_2OCF_2CF_3$ (XXII)

F^{19} nmr: 87.7 ∅* ($\underset{\sim}{C}F_3$, c), 88.8 ∅* ($CF_3\underset{\sim}{C}F_2$, c), 83.7 ∅* ($O\underset{\sim}{C}F_2CF_2CF_2\underset{\sim}{C}F_2$, c), 126.2 ∅* ($OCF_2\underset{\sim}{C}F_2\underset{\sim}{C}F_2CF_2O$, triplet, J = 152 c/s); Mol. Wt. 458 by mass spectral analysis.

Anal. Calcd. for $C_8F_{18}O_2$ (470.08): C, 20.4; F, 72.8. Found: C, 20.4; F, 73.0.

b. $CF_3CF_2OCF_2CF_2CF(CFO)OCF_2CF_2OCF_2CF_3$ (XXIV)

F^{19} nmr: 87.7 ∅* ($\underset{\sim}{C}F_3$, c), 88.8 ∅* ($CF_3\underset{\sim}{C}F_2$, c), 82.7 ∅* [$\underset{\sim}{C}F_2CF_2CF(CFO)$, c], 125 ∅* [$CF_2\underset{\sim}{C}F_2CF(CFO)$, c], 128.5 ∅* [$CF_2CF_2\underset{\sim}{C}F$-(CFO), c], AB at 83.6 and 92 ∅* [$CF(CFO)O\underset{\sim}{C}F_2$, J = 152 c/s], ν 5.3 μ (>=O). Mol. Wt. 520 (theory 564), by mass spectral analysis.

c. $(CF_3CF_2OCF_2CF_2)_2CFOCF_2CF_2OCF_2CF_3$ (XXV)

F^{19} nmr: $CF_3CF_2OCF_2$ as above, 122.5 ∅* ($\underset{\sim}{C}F_2CF$, c), 138.5 ∅* ($\underset{\sim}{C}F$, c), 85.2 ∅* ($CFO\underset{\sim}{C}F_2CF_2O$, c), 88.9 ∅* ($CFOCF_2\underset{\sim}{C}F_2$, c). Mol. Wt. 770 by VPO.

Anal. Calcd for $C_{13}F_{28}O_4$ (752.13): C, 20.7; F, 70.7. Found: C, 20.6; F, 70.3.

3.   Photolysis of $O[CF_2CF_2CFO]_2$ (XVIII)

The procedure for photodimerization of this compound was described in the discussion. Analytical data on the new compounds isolated from this reaction are given below.

a. $FOCCF_2CF_2OCF_2CF_2CF(COF)OCF_2CF_2OCF_2CF_2COF$ (XXVIII)

F^{19} nmr: -23.6 ∅* ($CF_2\underset{\sim}{C}OF$, complex 5-fold), 121.2 ∅* ($\underset{\sim}{C}F_2COF$, complex 4-fold), 85.5 ∅* ($\underset{\sim}{C}F_2CF_2COF$, c), 82 ∅*

[O$\underset{\sim}{C}$F$_2$CF$_2$CF(COF), c], 124.3 ∅* [OCF$_2$$\underset{\sim}{C}F_2$CF(COF), c], 127.9 ∅*
[$\underset{\sim}{C}$F(COF), c], -26.9 ∅* (CF$\underset{\sim}{C}$OF, c), 83.3 and 91.5 ∅* (CFO$\underset{\sim}{C}$F$_2$CF$_2$,
AB J = 149 c/s), 88.1 ∅* (CFOCF$_2$$\underset{\sim}{C}F_2$, c), ν 5.3 μ (>=O). Mol. Wt.
635 by mass spectral analysis, Eq. Wt. 202.5 (theory 203.5).

Anal. Calcd. for $C_{12}F_{20}O_6$ (620.12): C, 23.2; F, 61.3.
Found: C, 23.0; F, 61.1.

b. (FOCCF$_2$CF$_2$OCF$_2$CF$_2$)$_2$CFOCF$_2$CF$_2$OCF$_2$CF$_2$COF (XXIX)

F^{19} nmr: FOCCF$_2$CF$_2$ absorptions as above, 82.4 ∅*
($\underset{\sim}{C}$F$_2$CF$_2$CF, c), 122.5 ∅* (CF$_2$$\underset{\sim}{C}F_2$CF, c), 138.6 ∅* ($\underset{\sim}{C}$F, c), 85.8 ∅*
(CFO$\underset{\sim}{C}$F$_2$, c), 88.5 ∅* (CFOCF$_2$$\underset{\sim}{C}F_2$, c). Mol. Wt. 800 by VPO (on
the acid); Eq. wt. 280 (theory 278.7).

Anal. Calcd. for $C_{16}F_{28}O_7$ (836.16): C, 22.98; F, 63.62.
Found: C, 23.0; F, 62.5.

This compound contained a small absorption at 126 ∅*
indicating contamination with a compound containing the OCF$_2$CF$_2$-
CF$_2$CF$_2$O unit. The fact that a mixture of an authentic sample of
tetramer and (XXIX) eluted at the same time on VPC indicates that
some tetramer is probably present here.

c. FOCCF$_2$CF$_2$[O(CF$_2$)$_4$]$_2$OCF$_2$CF$_2$COF (Phototrimer)

F^{19} nmr data is given in the discussion.

4. Decarboxylative Fluorination of [CF$_2$CF$_2$OCF$_2$CF$_2$CO$_2$H]$_2$

A 9.0 g portion of POPF-D acid was placed in a teflon vessel
and the vessel connected in series to a NaF scrubber and a cooled
gas trap. A mixture of fluorine and nitrogen was passed at the
rate of 20 ml/min and 80 ml/min, respectively, into the stirred

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acid which was maintained at a temperature of 185°C. The off gases (5.5 g) were collected in the cooled gas trap. Vapor phase chromatography on a Kel-F Pentamer column, 6-1/2' x 1/4", separated the mixture (b.p. ~90°C) into two major peaks which were identified as (XXII) (74%) and (XXXIII) (22%).

a. $CF_3OCF_2CF_2CF_2CF_2OCF_2CF_3$ (XXXIII)
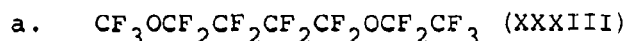
Structure assignment was based on F^{19} nmr: 55.9 ø* ($\underset{\sim}{CF_3}$O, triplet J = 8.9 c/s), 85.8 ø* ($O\underset{\sim}{CF_2}CF_2CF_2\underset{\sim}{CF_2}O$, c), 126.1 ø* ($OCF_2\underset{\sim}{CF_2}\underset{\sim}{CF_2}CF_2$, triplet, J = 7.6 c/s), OCF_2CF_3 as recorded above.

5.   Decarboxylative Fluorination of $HO_2CCF_2CF_2OCF_2CF_2CF-(CO_2H)OCF_2CF_2OCF_2CF_2CO_2H$
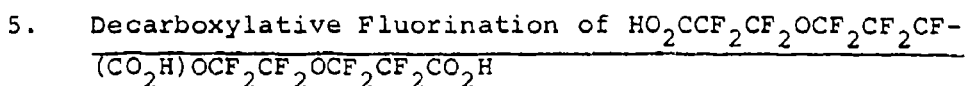
The procedure used was the same as that described for re-action of perfluoro-4,9-dioxadodecanedioic acid above. In this case, however, about 50% of the product consisted of unreacted acid. Fluorination of 10 g of acid gave 7 g of a mixture of unre-acted acid and inert fluorocarbon compounds which collected in a cooled gas trap. Distillation gave 4.0 g of material (b.p. ~105°C) which on chromatographic analysis on a Kel-F Pentamer column, (6-1/2' x 1/4") gave two major peaks identified as a mixture of (XXX) and (XXXI) (20%), (XXXII) (78%), and one unknown peak (2%).

a. $CF_3CF_2OCF_2CF_2CF_2OCF_2CF_2OCF_2CF_3$ (XXX)
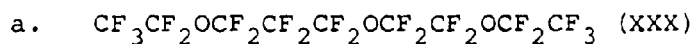
F^{19} nmr: CF_3CF_2 as above, 84 ø* ($O\underset{\sim}{CF_2}CF_2\underset{\sim}{CF_2}O$, c), 129.8 ø* ($OCF_2\underset{\sim}{CF_2}CF_2O$, c), 89 ø* ($O\underset{\sim}{CF_2}\underset{\sim}{CF_2}O$, c). Mol. Wt. 536 by mass spectral analysis.

Anal. Calcd. for $C_9F_{18}O_3$ (536.09): C, 20.7; F, 70.9. Found: C, 20.4; F, 70.3.

b. $CF_3OCF_2CF_2CF_2OCF_2CF_2OCF_2CF_3$ (XXXI) and
$\overline{CF_3CF_2OCF_2CF_2CF_2OCF_2CF_2OCF_3}$ (XXXII)
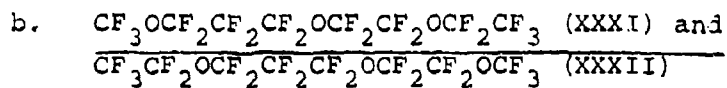
     Assuming a mixture of (XXXI) and (XXXII), all of the nmr absorptions are accounted for by peak positions and areas found. The peak assignments are presented in (i) and (ii) below. The required peak areas together with the actual measured peak areas are presented in (iii) below.

(i) $CF_3-O-CF_2-CF_2\cdot\cdot CF_2-O-CF_2-CF_2-O-CF_2-CF_3$

  ø*:   56   86   130 84   88.8 88.8 88.8 87.7

          (J = 8.3 c/s)

Calcd. Area: 3   2   2 2   6   3

(ii) $CF_3-CF_2-O-CF_2-CF_2-CF_2-O-CF_2-CF_2-O-CF_3$

  ø*:   87.7 88.8 84 130 84   88.8 90   56

        (J = 8.3 c/s)

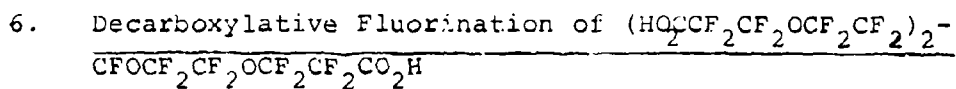Calcd.Area: 3   2   4   2   2   2   3

(iii)

  ø*:   56   84   86 87.7 88.8   90 130

  Σ Area: 6   6   2   6   10   2   4

  Found: 6   5.8 1.8 6.2 10.2   2   4

6.   Decarboxylative Fluorination of $\overline{(HO_2CCF_2CF_2OCF_2CF_2)_2-}$
$\overline{CFOCF_2CF_2OCF_2CF_2CO_2H}$

     Decarboxylative fluorination of (XXIXa) gave low yields (~10%) of inert compounds along with sizable quantities of COF_2. VPC of the inert compounds showed (XXV) as the major product along with smaller amounts of six other compounds.

7. Photopolymerization of $O[CF_2CF_2CFO]_2$

A solution of 27 g (.087 mole of POPF in 135 ml of FC-75 was added to a immersion-type quartz photoreactor and irradiated 2.5 hours with a 450 watt Hanovia lamp. Distillation at atmospheric pressure served to remove the FC-75 and unreacted POPF. The POPF was separated from the FC-75 by conversion to the methyl ester and distillation (6.7 g, .02 mole). Distillation of the original pot residue gave three fractions: fraction 1, b.p. 23-90°/14 mm (2 g); fraction 2, b.p. 23-75°/1 mm (1.8 g); and fraction 3, a viscous oil (?.^ g, $\overline{M}_n$ = 1000, Eq. Wt. = 382, f = 2.6). The combined distillate contained 25% photodimer, 12% (XXVIII), 36% phototrimer, 7% (XXIX), and 10% of four unknown compounds.

8. End-Capping Reactions

    a. Reaction of $CF_3(CF_2)_6CH_2OH$ with $SOCl_2$

Conversion of $HOCH_2(CF_2)_3CH_2OH$ to $ClCH_2(CF_2)_3CH_2Cl$ by reaction with $SOCl_2$ is reported to be a general reaction. However, our attempts to convert $CF_3(CF_2)_6CH_2OH$ to the chloride under various conditions gave what appears to be the sulfonyl chloride and sulfite ester rather than the desired alkyl chloride.

$CF_3(CF_2)_6CH_2SO_2Cl$, a clear colorless liquid, b.p. 45°C/1 mm.

Calcd. for $C_8H_2ClF_{15}O_2S$ (482.63): C, 19.91; F, 59.05; H, 0.42; S, 6.64. Found: C, 20.1; F, 59.8; H, 0.4.

$[CF_3(CF_2)_6CH_2O]_2SO$, a colorless solid with a m.p. at ca. room temperature.

Calcd. for $C_{16}H_4F_{30}O_3S$ (846.30): C, 22.71; F, 67.36; H, 0.48; S, 3.79. Found: C, 22.8; F, 67.5; H, 0.5.

b.   Reaction of $CH_3O_2C(CF_2CF_2OCF_2CF_2)_nCO_2CH_3$ with $C_6H_5NHCH_3$

A mixture of N-methylaniline (4.3 g, .04 mole), ester (7.1 g, .0047 mole based on a $\bar{M}n$ = 1800, and a f = 2.5), and 50 ml of CF_3CH_2OH was heated at reflux until the infrared showed no ester carbonyl (2 days). Removal of the solvent and excess aniline at 90°C/1 mm left a residue showing weak carbonyl. N-methylaniline and CF_3CH_2OH were added to the black tarry residue and refluxed over the weekend. Removal of solvent and excess aniline gave a black tarry residue with little apparent change in the C=O absorption from the initial reaction. Heat aging was carried out on this sample.

c.   Reaction of $CF_3CF_2OCF_2CF_2COX$ and $C_6H_{11}NC$

A mixture of 5.8 g (0.02 mole) of $CF_3CF_2OCF_2CF_2COCl$ and 1.0 g (.01 mole) of cyclohexyl isonitrile was heated at reflux for several days. The original N≡C absorption (I.R.) disappeared after about 24 hours and was replaced by one now equal in intensity to the COCl absorption band. Continued refluxing for 3-4 days produced no change in the intensity of the N=C or C=O bands or in the remainder of the spectrum. Reaction of $CF_3CF_2OCF_2CF_2COF$ and cyclohexyl isonitrile led to the same end product, presumably the α-addition product.

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13. ABSTRACT Photolysis of perfluoroether diacid fluorides and chain-extension of fluorocarbon ether-bridged chlorosilanes have been investigated as routes to a high-temperature integral fuel tank sealant polymer.

Photolysis of perfluoroether diacid fluorides has been found to give two triacid fluorides by reaction of the initially formed photo-fragments with the monomer diacid fluoride. These triacid fluorides lead to large quantities of branched polymer and prevent formation of high molecular weight linear polymer.

Six different fluorocarbon ether-bridged chlorosilanes have been prepared and their polymerization to silanol-ended fluorocarbon ether-bridged siloxanes investigated.

Sealant compounds prepared from the siloxane polymers have long term stability in air up to 400°F. Substitution of trifluoropropyl groups on silicon is necessary to achieve the desired jet fuel resistance. Aging of two sealant compounds containing trifluoropropyl groups on silicon indicate that they will be useful for certain periods of time up to 500°F in a jet fuel environment. However, more research is necessary to firmly determine the upper temperature limit.

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